VISIT…

# 27
# Metalworking Fluids

**William L. Brown**
*Union Carbide Corporation*
*Tarrytown, New York*

## I. OVERVIEW

Metalworking is a major industry in the United States today. Metalworking operations include rolling, forging, stamping, drawing, forming, cutting, and grinding. Practically all metal objects, from structural steel beams to screws, have undergone at least one metalworking operation.

The success of most metalworking operations is dependent on the use of good lubricants and coolants. There are a large variety of these metalworking fluids. They include fatty acid based soaps, formulated hydrocarbons, emulsified oils, and aqueous solutions. These products are used in operations ranging from the drawing of wire to the tapping of nut threads. In each case, the metalworking fluid has been adapted to satisfy the needs of a specific application.

This chapter reviews the uses of synthetic lubricants in various metalworking operations. It begins by defining metalworking and metalworking fluids. A brief review of the history of metalworking fluids is then presented, with particular attention to the incorporation of synthetic lubricants.

The synthetic lubricants currently being used in metalworking fluids are defined. These products include polyalkylene glycols, esters, and synthetic hydrocarbons. The generic structures of these synthetic lubricants are illustrated, and the physical properties that have led to their incorporation in metalworking fluids are described.

This chapter focuses on the use of polyalkylene glycols in metalworking fluids. Polyalkylene glycols are of importance to the metalworking industry because of their unique solubility properties in water. The mechanism of how they work is described, and a number of applications are presented. The use of other synthetic lubricants in metalworking fluids is then reviewed.

The remainder of the chapter examines the future of synthetic lubricants in the metalworking industry. In addition, since health and disposal regulations and the need for improved workpiece quality affect the use of synthetic lubricants in metalworking fluids, these factors are discussed.

The metalworking industry is very large and diverse. Metalworking fluid formulations are tailored to specific operations and locations. Formulations are affected by such factors as production speeds, inventory turnover, local water quality, ambient weather conditions, and effluent



Copyright © 1999 Marcel Dekker, Inc.

regulations. Therefore, this chapter gives an overview of the uses of synthetic lubricants in the metalworking industry, without attempting to provide exhaustive detail.

## II. DEFINITIONS

Metalworking is the shaping of a metallic workpiece to conform to a desired set of geometric specifications. Metalworking can be divided into two basic categories, cutting and forming. In cutting operations, the blank is shaped by removing unwanted metal in the form of discrete chips. Cutting operations include turning, tapping, milling, broaching, and grinding. Metal-forming processes involve the plastic deformation of the workpiece into a desired shape. Drawing, hot and cold rolling, stamping, and forging are examples of metal-forming operations.

In both cutting and forming operations, the metalworking fluid plays a critical role. The two most important functions of the metalworking fluid are to provide adequate lubrication between the workpiece and the tool or die and to remove the heat that is generated [1].

Lubrication can be defined as the reduction of friction between two moving surfaces. In metalworking operations, lubrication can be divided into two types, hydrodynamic and boundary, or extreme pressure (EP). In hydrodynamic lubrication, the moving surfaces are always separated by a film of fluid or lubricant. Both the film thickness and the coefficient of friction are functions of the parameter $ZN/P$, where $Z$ is the lubricant's dynamic viscosity, $N$ represents the relative velocity of the moving surfaces, and $P$ is the applied load per unit area [2,3]. The higher the velocity or the more viscous the lubricant, the thicker the fluid film. The coefficient of friction will also increase because of an increase in viscous drag. Conversely, increasing the load or pressure will decrease the film thickness and the coefficient of friction as long as hydrodynamic conditions are maintained.

Boundary, or EP, lubrication is necessary when the pressures experienced are great enough to cause contact between the moving metal surfaces. The purpose of boundary or EP additives is to minimize the wear experienced when the surfaces rub against each other.

Boundary lubricant additives are polar compounds like fatty alcohols, acids, and esters, which adsorb onto the metal surfaces forming thin, low shear strength films. These solid films help prevent metal–metal contact and reduce friction and wear [2,4].

The EP lubricity additives used in metalworking operations are usually organic compounds that contain phosphorus, chlorine, or sulfur. During the metalworking process, these additives react with the metal surfaces forming organic or organometallic films [2,4]. These films then act to reduce the force necessary to slide the surfaces past one another, while at the same time minimizing wear [5].

Cooling is the other critical function of a metalworking fluid. The transfer of heat away from the tool or die is affected by the specific heat and the heat of vaporization of the metalworking fluid. The specific heat is the amount of heat required to raise the temperature of one gram of fluid one degree Celsius. The larger this value, the more heat the fluid can absorb for an incremental temperature rise, resulting in more efficient cooling. The heat of vaporization is the amount of heat required to vaporize a gram of liquid. A fluid with a high heat of vaporization will also cool efficiently, since it absorbs large amounts of energy as it transforms from a liquid to a gas. Heat transfer in metalworking can also be affected by the fluid's boiling point, ambient temperature [5], viscosity, surface energy, and application method.

Good lubrication and cooling will prolong tool or die life, improve surface finishes, and permit higher production speeds. The cooling and lubricating properties of a metalworking fluid must be matched to the operation being performed. In high cutting speed operations like turning and grinding, cooling is of paramount importance. However, in lower speed operations that

Copyright © 1999 Marcel Dekker, Inc.

involve heavy cuts or large deformations, the lubricating properties of the metalworking fluid are critical [6].

In addition to providing adequate lubrication and cooling, metalworking fluids must protect the machine and the workpiece from corrosion and must remove chips from the cutting zone. It is also important that the metalworking fluid be benign and nonirritating to the operator.

There are four major classes of metalworking fluids. These different types are defined in Sections II. A-II.D.

## A. Straight Oils

The products known as straight oils are derived primarily from petroleum fractions, although animal and vegetable oils are occasionally used [6]. Synthetic lubricants can also be employed as straight oil base stocks. These base stocks, whether natural or synthetic, are usually compounded with various boundary and EP lubricity additives. Straight oil metalworking fluids contain no water and are sold "ready to use." They are excellent lubricants but have limited cooling capacity.

## B. Soluble Oils

Soluble oils are actually oil-in-water emulsions that take advantage of the lubricity of oils and the cooling properties of water. This is a very versatile class of metalworking fluids. In severe cutting or forming operations, they are usually formulated with chlorine- and sulfur-containing extreme pressure lubricity additives and diluted only one to five times with water [7]. However, in light cutting or grinding operations, the soluble oil concentrate often contains only rust inhibitors and can be cut 20 to 100 times with water.

## C. Chemical Solutions (Synthetics)

Chemical metalworking fluids contain no petroleum oil and form true solutions when diluted with water. These metalworking fluids are often referred to as "synthetics." However, not all "synthetic" metalworking fluids contain synthetic lubricants as these are defined later in this chapter. Synthetic lubricants include polyalkylene glycols, various esters, and polyolefins. Therefore, to avoid confusion in this chapter, these oil-free, water-soluble products are referred to as "chemical metalworking fluids" or "chemical solutions."

Chemical solutions were originally formulated for grinding and light-duty cutting operations. However, the incorporation of synthetic lubricants and the development of improved water-soluble boundary and EP lubricity additives greatly expanded the utility of this class of metalworking fluids.

## D. Semichemical Solutions (Semisynthetics)

Semichemical metalworking fluids are an attempt to get the best properties of both soluble oils and chemical solutions. According to the most common definition, a semichemical metalworking fluid is a product whose concentrate contains water-soluble additives, emulsifiers, and less than 20% petroleum oil [8].

# III. HISTORICAL DEVELOPMENT

The use of lubricants dates back to the times of the ancient Egyptians, who used fats to grease chariot wheels [9]. However, the use of lubricants in metalworking operations is relatively recent. One of the earliest references to metalworking lubricants comes from the writings of Birin-

Copyright © 1999 Marcel Dekker, Inc.

guccio, who observed in the early 1500s that it is important to use wax when drawing high quality gold and silver wire [10]. The widespread use of metal working fluids, however, coincided with the Industrial Revolution, which began in England in the late eighteenth century [2].

By the mid-nineteenth century, mineral oils were being widely used as metalworking lubricants [2]. W. H. Northcott observed in 1868 that the use of oils as metalworking fluids greatly improved cutting speeds and tool life, reduced power consumption, and produced smoother cuts [11]. Northcott also described how soda water worked well as a metalworking fluid despite some corrosion problems.

The development of high speed cutting tools and the increased use of grinding began to show the limitations of oils as metalworking lubricants [2]. Most of the energy used to cut or grind a metal workpiece is dissipated as heat [4,8,12]. Thus, as cutting speeds increased, the cooling properties of the metalworking fluid became more important. While oils are excellent lubricants, their cooling capacity is limited. The use of oil-based metalworking fluids in higher speed operations resulted in poor tool life and the generation of irritating smoke and fumes [13,14].

In 1883 Taylor demonstrated the importance of water as a base for metalworking fluids. Many years later, he published a report of this work, in which he had showed that by using water as a metalworking fluid, cutting speeds could be increased by 30–40% [15]. This increase in speeds is possible primarily because of the excellent cooling properties of water relative to hydrocarbon oils. Water has a higher specific heat and heat of vaporization than hydrocarbon oils, accounting for its superior cooling ability [16].

By the end of the nineteenth century, the use of water to flood the cutting tool was quite common [12]. However, as a metalworking fluid, water has two obvious drawbacks. First, water is a poor lubricant. Second, the use of water leads to the corrosion of both the tool and the workpiece [17].

The first attempts to solve these shortcomings occurred at the turn of the century. Sodium carbonate, or soda ash, was added to inhibit corrosion, and phosphates and soaps were included for lubricity enhancement [12,14]. Over time, however, the soda ash tended to drop out of solution, depositing on machinery and thereby preventing smooth operation [12]. Also, about the same time, mixtures of oils and water, loosely coupled by alkali, were being used to improve the performance of water as a metalworking fluid. Unfortunately, these systems did not adequately control corrosion and were inherently unstable [12].

Good quality soluble oils were first developed in the 1920s [12,14]. They quickly became the dominant form of water-based metalworking fluid, although solutions containing sodium carbonate continued to be used in grinding operations through the 1950s [12,14]. Soluble oils effectively take advantage of the cooling properties of water while providing good lubricity and corrosion protection. The use of soluble oils instead of neat hydrocarbon-based metalworking fluids enabled manufacturers to increase their production rates without significant sacrifices in surface finish or tool or die life.

The use of soluble oils grew quickly at the expense of neat hydrocarbon metalworking fluids during the middle of this century. Besides being better coolants, soluble oils offer a number of other advantages. Soluble oils are cleaner than straight oil metalworking fluids. They do not fume or smoke significantly, and the risk of fire hazard is greatly reduced [7]. Also, it is easier to remove soluble oil residues from the machinery and the workpiece.

Another major factor that led to the growth of soluble oils is their versatility. The lubrication and cooling properties of soluble oil metalworking fluids can be adjusted by simply altering the dilution ratio or changing the type or amount of lubricity additives. In heavy-duty forming operations, the soluble oil concentrate can be formulated with high concentrations of chlorine-,

Copyright © 1999 Marcel Dekker, Inc.

sulfur-, or phosphorus-containing extreme pressure lubricity additives and diluted only 1:1 or 1:2 with water prior to use [7]. However, soluble oils diluted 20:1 to 100:1 with water are also used in high speed, light-duty cutting and grinding operations. These light-duty products are often formulated with rust inhibitors only.

A further advantage of soluble oils relative to neat hydrocarbon-based metalworking fluids is cost. Although a soluble oil concentrate is more expensive than an equivalent volume of straight oil metalworking fluid, the actual cost is significantly reduced by the dilution of the concentrate with water. Also, soluble oils are less prone to losses from dragout than straight oils, which results in lower fluid makeup costs [14].

Despite their obvious advantages, soluble oils did present some new problems. The most significant drawback associated with soluble oils is their susceptibility to bacterial attack. Microorganisms living in the water quickly learn to metabolize the emulsified organic compounds. They rapidly multiply, releasing unpleasant odors and eventually splitting the emulsions by metabolizing the surfactants and lowering the fluid's pH [12]. While the incorporation of biocides can reduce the magnitude of this deficiency, biological attack is still the biggest problem faced by the users of soluble oils.

Soluble oils presented several other problems. Soluble oils tend to emulsify tramp gear lubricants or hydraulic fluids, which can adversely affect the performance of the metalworking lubricant. Also, soluble oil metalworking fluids are sensitive to water quality, especially pH and hardness [18].

In the early 1950s the users of grinding solutions containing soda ash began to find substitutes that provided good corrosion protection without forming troublesome deposits [12]. These alternative corrosion inhibitors were based mostly on alkali nitrites, organic amines, or amine-neutralized organic acids [12,14,19]. These new solutions, referred to as chemical or synthetic metalworking fluids because they contained no petroleum oil, were quite successful. They provided good corrosion protection, excellent cooling, and adequate lubricity. They were also clean, very stable, and more resistant to biological attack than soluble oil metalworking fluids [5].

Because of their initial success as grinding coolants, and the continuing search for cutting and forming lubricants that were more trouble free than soluble oils, chemical metalworking fluids were tried in a number of more demanding cutting operations such as turning, milling, and tapping [14]. Their performance in these operations was promising enough to encourage further development. The inclusion of water-soluble lubricity additives such as fatty acids, phosphate acid esters [20], and polyalkylene glycols significantly enhanced the lubricity of chemical metalworking fluids. Chemical metalworking fluids were soon being used in many cutting operations as well as applications involving light- and medium-duty drawing and forming [14,19].

Chemical metalworking fluids offered a number of advantages over traditional soluble oils. These advantages, which still exist today, are summarized in the paragraphs that follow.

1. *Biological stability.* While biocides are still needed for optimum performance, chemical metalworking fluids are generally more resistant to biological attack than soluble oils [5]. This increased biological stability results in less odor, better pH control, and longer sump life [5,12]. Longer fluid life means reduced raw material and disposal costs.
2. *Solution stability.* Chemical metalworking fluids can be formulated to have good hard water stability and to be resistant to pH variations [18]. They are also less prone to drag out than soluble oils, resulting in less coolant use and cleaner chips or swarf [12].
3. *Cooling.* Chemical metalworking fluids are significantly better coolants than soluble oils [5,21]. Better cooling means longer tool life and higher production speeds.
4. *Cleanliness.* The clarity of chemical metalworking fluids is very good, resulting in excellent workpiece visibility [5,14]. Not only are these products clear initially, but their ability

Copyright © 1999 Marcel Dekker, Inc.

to reject tramp gear and hydraulic oils helps them remain transparent [18]. Chemical metal-working fluids also produce smaller amounts of oily residues on the machines and floor, thereby greatly reducing the risk of a fall [14].

However, chemical metalworking fluids were not a panacea. They presented the metal-working industry with the following problems.

1. *Slideway lubrication.* Many chemical metalworking fluids, because of their good detergency, tend to wash away slideway lubricants, causing significant operational problems. Also, some chemical metalworking fluids can, over time, cause the machine's moving parts to stick. This sticking can be the result of water evaporating from some isolated coolant, leaving behind the more viscous corrosion inhibitors and lubricity additives. However, it can also be due to the deposition of additives, which react with the calcium and magnesium ions in hard water to form insoluble residues [14]. Gummy residues can also be formed when fluids containing amine borate corrosion inhibitors are used in hard water [22].

Over the years it has been found that slideway lubrication problems can be reduced by reformulating the concentrate with lower viscosity components that have good hard water stability and less detergency. Also, the use of detergent-resistant slideway lubricants and a more comprehensive machine lubrication program can help alleviate these problems [12].

2. *Machine lubrication.* Upon switching from soluble oils to chemical metalworking fluids, some operators discover that their machinery is no longer being adequately lubricated. Because chemical metalworking lubricants by definition contain no hydrocarbons, they do not leave a residual oil film on the machine's moving parts [5]. This problem can often be solved by following a routine machine lubrication program [12].

3. *Dermatitis.* Because of their good detergency and high pH, chemical metalworking fluids can wash away the skin's natural oils, resulting in dermatitis [8]. The use of barrier creams or rubber gloves, along with the practice of good industrial hygiene, can help overcome this problem.

4. *Paint and seal compatibility.* Some of the components in chemical coolants can attack the seals and paints used in metalworking machinery. Resistant paints and seals are now available and can be found in much of the newer machinery [12].

5. *Lubricity and corrosion.* While insufficient lubricity and corrosion protection limited the use of early chemical metalworking fluids, the development of improved water-soluble additives has greatly expanded the utility of these products. They can now be employed in many of the applications that are currently using soluble oils.

The problems associated with chemical metalworking fluids, especially those pertaining to machine and slideway lubrication, led to the development of semichemical metalworking fluids. These products typically contain up to 20% hydrocarbon oil in their concentrate as well as surfactants, amines, and other water-soluble additives. Semichemical fluids were well established by the mid-1960s [5], and they are currently enjoying an increase in popularity. However, while they strive to incorporate the better machine lubrication of soluble oils, they also lose some of the bacterial resistance inherent in chemical metalworking fluids [12]. In short, semichemical products, as their name suggests, are a compromise between soluble oils and chemical metalworking fluids.

By 1971, 33% of the metalworking fluids sold into cutting and grinding applications were soluble oils, chemical fluids, or semichemical products [23]. However, these fluids are sold as concentrates which, on average, are diluted about 20 times with water. Thus, approximately 90% of all metal removal operations were using water-based metalworking fluids [24].

Both chemical and soluble oil metalworking fluids have undergone significant formulation changes over the past 20 years in response to toxicity concerns.

Copyright © 1999 Marcel Dekker, Inc.

In the late 1960s the presence of nitrosamines in chemical metalworking fluids was discovered. Nitrosamines can be formed by reactions between nitrites and monoethanolamine or diethanolamine. Particular attention was given to the discovery of *N*-nitrosodiethanolamine (NDELA) in metalworking fluids. NDELA is a potent carcinogen to rats and hamsters [25], and it is known to be absorbed through human skin [26]. Because of concerns about the exposure of machinists to NDELA, much work was done during the mid-1970s to find replacements for sodium nitrite [22]. The best substitutes were found to be amine borates or the salts of organic acids and amines. By 1980 the use of nitrites in metalworking fluids had been essentially eliminated.

In the mid-1980s, oils containing polynuclear aromatics were identified as potential carcinogens. As a result, practically all oil-containing metalworking fluids were reformulated. These products now incorporate severely hydrotreated hydrocarbons as lubricant base stocks [27].

Toxicity continues to be a major issue affecting the use of the various types of metalworking fluid. The other factors currently shaping the metalworking fluid industry are waste minimization, disposal, environmental regulations, and workpiece quality.

## IV. SYNTHETIC LUBRICANTS

Synthetic lubricants are defined as products made from the controlled combination of discrete compounds. This distinguishes them from refined petroleum products. The major classes of synthetic lubricants used in metalworking operations are described in Sections III.A—III.E.

### A. Polyalkylene Glycols (PAGs)

The diverse class of synthetic lubricants known as PAGs is made from the polymerization of alkylene oxides, as shown in Fig. 1. The starter is usually an alkyl alcohol or a diol, but branched polymers are also made by alkoxylating triols or polyols. The oxide feed can be all ethylene oxide ($R' = H$), all propylene oxide ($R' = CH_3$), or mixtures of the two. Higher molecular weight monomers like butylene oxide can also be polymerized, but the commercial use of these products is very limited. The oxide feeds can be either mixed, resulting in a random polyalkylene glycol, or sequential, yielding a blocked structure. Blocked polyalkylene glycols are more surface active than the random polymers, but they are also much more likely to foam.

Polyalkylene glycols can be either soluble or insoluble in water, depending on the ratio of ethylene oxide to propylene oxide in the monomer feed. At room temperature, polyalkylene glycols made from a monomer feed consisting of more than approximately 20% ethylene oxide are water soluble. Polyalkylene glycols that contain less than 20% polymerized ethylene oxide show good solubility in hydrocarbons.

Water-soluble polyalkylene glycols have been used extensively in chemical and semichemi-

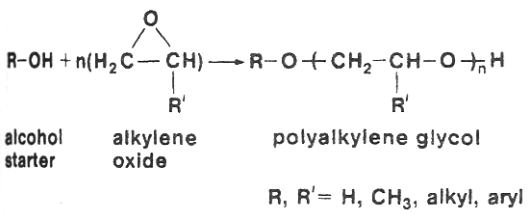



**Figure 1** Polyalkylene glycols.

Copyright © 1999 Marcel Dekker, Inc.

cal metalworking fluids [24,28–30]. Oil-soluble polyalkylene glycols have been employed in both semichemical and straight oil metalworking fluids as lubricity additives [31]. They have also been used neat in applications where their excellent water washability, resistance to staining or sludge formation, or clean burn-off characteristics are important [32–35].

## B. Esters

Esters are made from the condensation of organic acids and alcohols. This is a very diverse class of compounds, and the physical properties vary greatly depending on the acids and alcohols used. The most common classes of esters are monobasic acid esters, dibasic acid esters, polyol esters, and polyalkylene glycol esters (PAG esters). The generic structures of these compounds are shown in Fig. 2.

Monobasic acid esters and polyalkylene glycol esters are widely used in the metalworking industry. Monobasic acid esters such as methyl and butyl stearate and hexyl laurate have long been employed as lubricity additives in metalworking fluids [2,32]. In hydrocarbon-based products, these esters help reduce the interfacial tension between the oil and the metal surface, thereby increasing the ability of the fluid to penetrate between the workpiece and the tool or die [5]. In water-based products, monobasic acid esters are most commonly used as additives in the hydrocarbon phase of soluble oil or semichemical metalworking fluids, where they serve as boundary lubricants and corrosion inhibitors.

Polyalkylene glycol esters are used in chemical or semichemical metalworking fluids because of their solubility or good dispersity in water [36,37]. They are usually made from polyalkylene glycol diols, but monol- and polyol-started polyalkylene glycols can also be used. Polyalkylene glycol esters provide good lubricity and are synergistic with many corrosion inhibitors.

Two new polymeric esters have recently been commercialized for use in metalworking operations. One type, referred to as "complex polymeric esters," is based on pentaerythritol and runs to high molecular weights, ranging from 150,000 to over 2 million [38]. These high molecular weight liquids have been designed to enable the replacement of sulfur- and chlorine-containing extreme pressure additives in soluble oil metalworking fluid formulations.

Synthetic lubricants of the second type recently designed for use in metalworking fluids are "double-comb polymer esters." These esters are made by reacting butanol with α-olefin dicarboxylic acid copolymers [39]. These molecules have a double-comb structure, with the ester groups in the form of short side chains off a long hydrocarbon backbone. These polymeric esters range in molecular weight from 1200 to 2500. They have been used as lubricity additives in both neat oil and soluble oil systems.

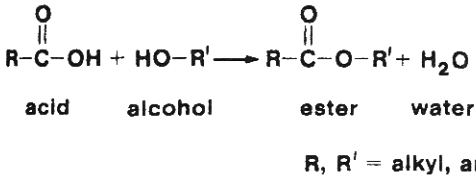
## C. Phosphate Esters

Phosphate esters are formed by reacting alcohols with phosphoric acid as shown in Fig. 3. Phosphate esters are used as synthetic lubricants in fire-resistant hydraulic fluids because of their resistance to burning [40]. However, these synthetic lubricant base stocks have not found any significant use in metalworking applications.

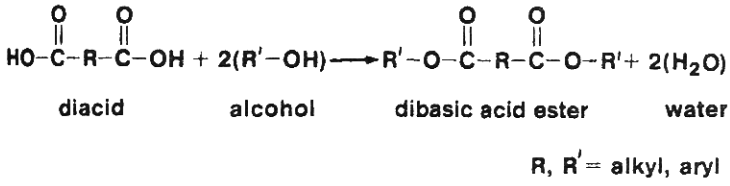
Phosphate esters are widely used in metalworking fluids as EP lubricity additives [2,5,6,32,41,42]. Oil-soluble phosphate esters like tricresyl phosphate are well-known lubricity additives and are commonly used in straight oil and soluble oil metalworking fluids. Water-soluble phosphate esters can be made by reacting ethoxylated alcohols with phosphoric acid. These products are often used as lubricity additives in chemical metalworking fluids [6,30].

Copyright © 1999 Marcel Dekker, Inc.

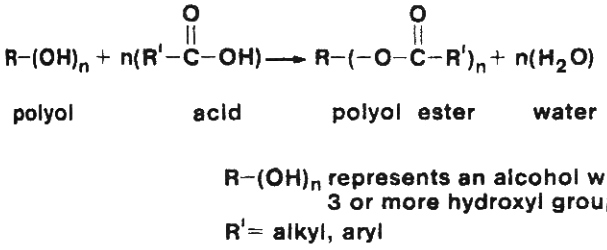
**Monobasic acid esters:**




**Dibasic acid esters:**




**Polyol esters:**




**Polyalkylene glycol esters:**

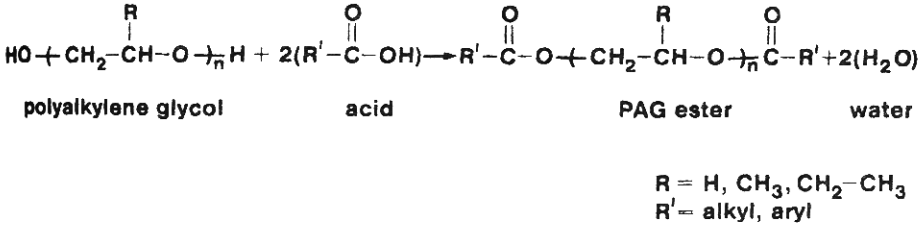



**Figure 2** Structures of some esters that are used as synthetic lubricants.

## D. Synthetic Hydrocarbons

Synthetic hydrocarbons are made from the combination of olefins through their double bonds. The most common synthetic hydrocarbons are poly (α-olefins), dialkybenzenes, and polyisobutylenes. The generic structures of these three synthetic hydrocarbon types are shown in Fig. 4.

Of these three classes of synthetic hydrocarbons, only polyisobutylenes have found significant use in the metalworking industry. Their primary applications have been as nonstaining thickeners [2] and as base oils for high temperature forming operations [32].

Copyright © 1999 Marcel Dekker, Inc.

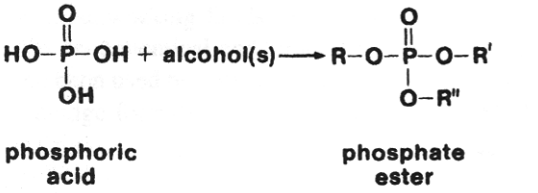
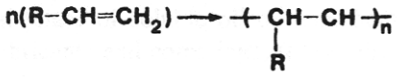
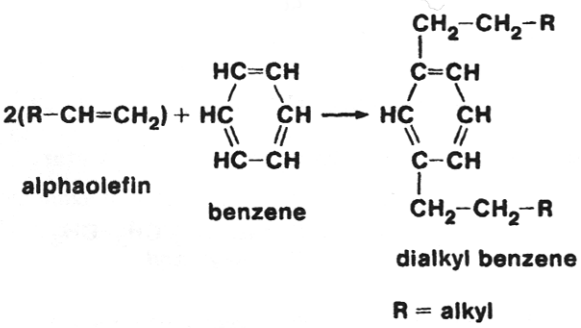



**Figure 3** Phosphate esters.

**Polyalphaolefins:**




**Dialkyl benzenes:**




**Polyisobutylenes:**

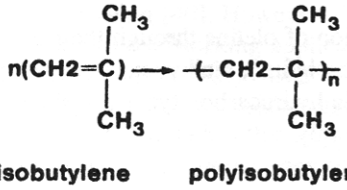



**Figure 4** Structures of some common synthetic hydrocarbons.

Copyright © 1999 Marcel Dekker, Inc.

Recently, α-olefins have been used in a variety of metalworking operations in conjunction with paraffinic base stocks. Metalworking fluids containing an equal blend of paraffin and α-olefin base stocks provided better lubricity and improved surface finishes relative to tests run with the paraffinic-based control [39].

### E. Other Synthetic Lubricants

Other synthetic lubricants and polymers have found use in metalworking operations. Polyacrylonitriles [43], styrene/maleic anhydride copolymers [44,45], and polyacrylamides [46] have all been documented as providing good lubricity in water-based metalworking fluids. Polyvinylpyrrolidones, polyvinyl alcohols, and copolymers of acrylic acid or methacrylic acid and an acrylic ester have also been cited as lubricity additives for use in chemical metalworking fluids [47]. However, the commercial use of these synthetic polymers is small. Also, a number of thermoplastic polymers have been used as solid lubricants in forming operations. A review of these polymers is presented by Schey [2]. However, the use of solid lubricants is not covered in this chapter.

## V. SYNTHETIC LUBRICANTS IN CHEMICAL METALWORKING FLUIDS

The most significant use of synthetic lubricants in the metalworking industry is in chemical solutions. The use of polyalkylene glycols in conjunction with water-soluble boundary or EP lubricity additives can significantly enhance the lubricity of chemical metalworking fluids, allowing them to effectively compete with soluble oils in a variety of cutting and forming operations.

### A. Polyalkylene Glycols in Chemical Metalworking Fluids

Polyalkylene glycols have a number of characteristics that make them ideal for use in chemical metalworking fluids. These properties include water solubility, inverse solubility, and cloud point [24].

Polyalkylene glycols can be synthesized that are soluble in water in all proportions. They are hydrolytically stable and are essentially unaffected by water quality or hardness.

In addition, polyalkylene glycols exhibit the property referred to as "inverse solubility," a characteristic of ethoxylated materials. As the temperature of an aqueous polyalkylene glycol solution increases, the solubility of the polyalkylene glycol in water decreases. Above a temperature known as the cloud point, the polyalkylene glycol will come out of solution, forming a hazy or cloudy dispersion. A 1% solution of a polyalkylene glycol below and above its cloud point is shown in Fig. 5.

The cloud point of a polyalkylene glycol is dependent on a number of factors. These include the polymer's ratio of ethylene oxide to propylene oxide, the starter, the end groups, and molecular weight. Cloud point is also affected by the polyalkylene glycol concentration and the presence of other water-soluble compounds. In particular, the cloud point of polyalkylene glycols can be lowered by the presence of ionizing salts. The high temperature insolubility of polyalkylene glycols can be used to greatly enhance the lubricating ability of chemical metalworking fluids.

Additional characteristics of PAGs that are advantageous; in chemical metalworking fluids are briefly listed as follows:

*Nonionic behavior.* Because polyalkylene glycols are nonionic, they can be used in combination with either cationic or anionic additives.

Copyright © 1999 Marcel Dekker, Inc.

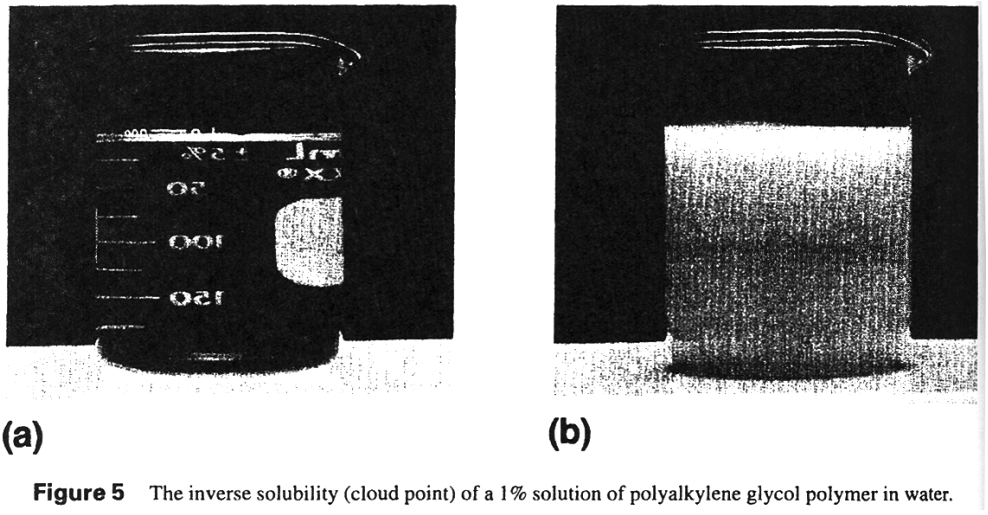



**Figure 5** The inverse solubility (cloud point) of a 1% solution of polyalkylene glycol polymer in water.

*Low reactivity.* Polyalkylene glycols are noncorrosive to commonly used metals.

*Liquid residues.* Because polyalkylene glycols are stable and water soluble, their residues are liquid and, if necessary, easily removed from machinery [24].

*Resistance to biological attack.* While polyalkylene glycols are biodegradable, their degradation rates are slow relative to those of fatty acids, phosphate esters, and many commonly used surfactants. This bioresistance leads to easier fluid maintenance and longer sump life, and thus lower raw material and disposal costs.

*Low toxicity.* Polyalkylene glycols exhibit low toxicity. However, as with all chemicals, the Material Safety Data Sheets should be studied before the product is used.

A typical formulation for a metalworking fluid employing a polyalkylene glycol is shown in Table 1. For typical cutting operations, this type of formulation is usually diluted 10:1 to 30:1 with water. It can also be used at much higher concentrations. For severe drawing operations, dilutions of 1:1 of 2:1 with water might be used. For light grinding, dilutions up to 50: 1 have been employed.

**Table 1** Typical Chemical Metalworking Fluid Formulation

| Component | Amount (wt %) |
|---|---|
| Polyalkylene glycol | 10–15 |
| Phosphate ester (or fatty acid) | 5–10 |
| Sulfurized fatty acid | 0–5 |
| Nonnitrite corrosion inhibitor | 15 |
| Triethanolamine | 10–15 |
| Biocide | —[a] |
| Water | 45–60 |

[a] Biocide added at concentrations recommended by the manufacturer.

Copyright © 1999 Marcel Dekker, Inc.

The purpose of the polyalkylene glycol is to provide hydrodynamic lubricity and inverse solubility. The fatty acid or phosphate ester provides enhanced wetting and boundary lubrication. The phosphate ester also has EP lubricating properties. In severe metalworking operations, a water-soluble, sulfur-containing compound may be necessary for added EP lubricity. The nonnitrite inhibitor is to protect both the machine and the workpiece from corrosion. Triethanolamine serves as an inexpensive corrosion inhibitor by keeping the pH of the solution elevated, typically between 8.5 and 9.2. The ethanolamine also helps to solubilize some of the lubricity additives. Biological attack is retarded through the use of biocides. Other additives such as antifoams, dyes, and chelating agents can be added if needed.

The key to the effectiveness of polyalkylene glycols in chemical metalworking fluids is their inverse solubility. The following mechanism, illustrated in Fig. 6, has been used to describe the role of the inverse solubility of polyalkylene glycols in metalworking fluids [2,24,30,48]:

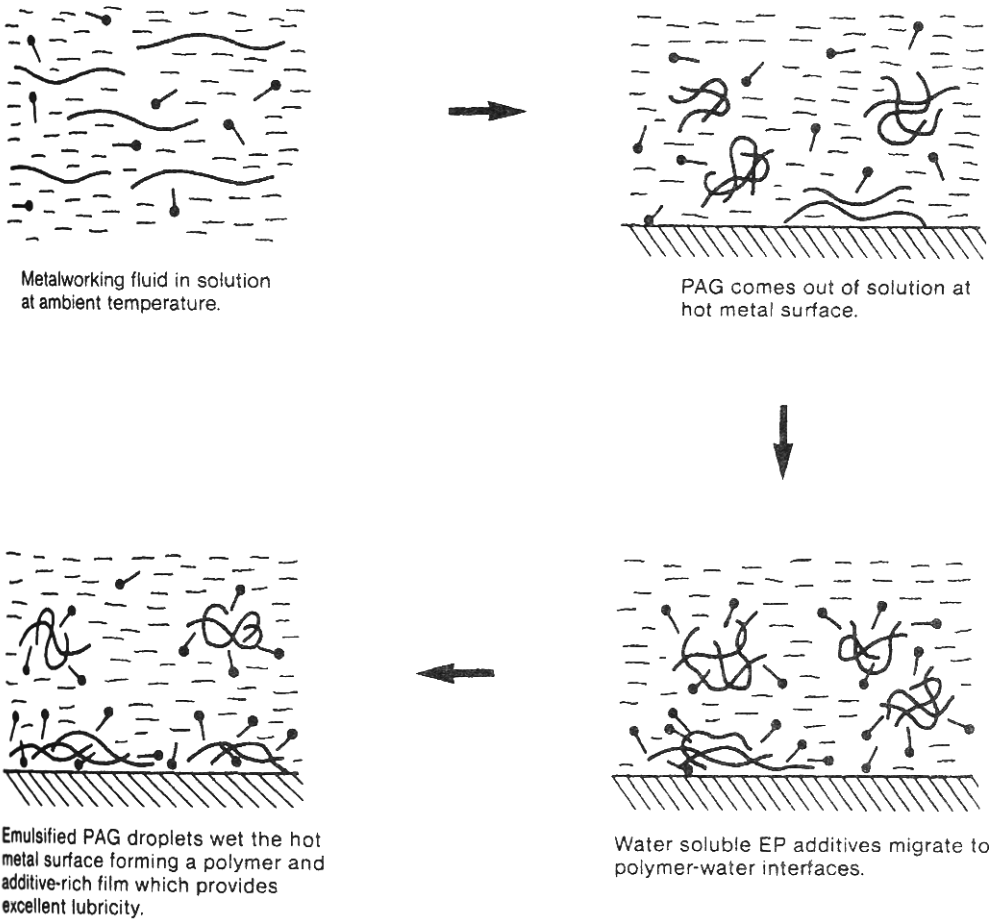

Metalworking fluid in solution at ambient temperature.
PAG comes out of solution at hot metal surface.
Water soluble EP additives migrate to polymer-water interfaces.
Emulsified PAG droplets wet the hot metal surface forming a polymer and additive-rich film which provides excellent lubricity.

**Figure 6** The inverse solubility (cloud point) mechanism of chemical metalworking fluids containing polyalkylene glycols.

Copyright © 1999 Marcel Dekker, Inc.

Cloud Point Mechanism of Polyalkylene Glycol Containing Chemical Metalworking Fluids

1. At ambient temperatures, typical of those found in a machine sump, the metalworking fluid is completely soluble in water, forming a clear, transparent solution.
2. The metalworking fluid is brought into contact with the hot tool or die. The temperature of the fluid is elevated above the cloud point of the polyalkylene glycol, causing the polymer to come out of solution and form small, oil-like drops.
3. The lubricity additives in the metalworking fluid are surface active and collect at the interface between the polyalkylene glycol and the water phases.
4. These polyalkylene glycol drops then preferentially wet the surfaces of the workpiece and the tool or die, much like the emulsified hydrocarbon droplets in a soluble oil metalworking fluid. The result is the formation of a thin layer of concentrated polyalkylene glycol and lubricity additives. This polyalkylene glycol film has excellent lubricating properties. The ability of the polyalkylene glycol to concentrate the polar lubricity additives at the tool or die surface helps explain the synergy often noted between these products [6,24,30].
5. The spent chips and excess metalworking fluid fall back into the relatively cool machine sump, where the polyalkylene glycol goes back into solution. In contrast, the chips generated during the use of soluble oils are coated with a significant amount of hydrocarbon lubricant that does not reemulsify. As a result, less lubricant is lost due to dragout when a chemical metalworking fluid is used.

Chemical metalworking fluids that do not contain polyalkylene glycols rely on their water-soluble additives coming in contact with the surface of the workpiece to achieve sufficient lubricity. The probability of this occurring is a function of the concentration of these lubricity additives. The addition of polyalkylene glycols, because of their inverse solubility, serves to concentrate the lubricity additives at the point of cut, or in the case of a drawing or forming operations, at the hot surface of the die. Also, the polyalkylene glycol itself is an excellent hydrodynamic lubricant. Better lubricity can therefore be achieved at the same product dilution ratio when polyalkylene glycols are used in conjunction with water-soluble boundary or EP additives.

While the presence of polyalkylene glycols improves the efficiency of lubricant delivery to the hot surfaces of the workpiece and the tool or die, it is important to remember that the mechanism of these chemical metalworking fluids is temperature activated. At ambient temperatures the lubricity of chemical metalworking fluids that contain polyalkylene glycols is greatly reduced. Because they contain no oil, these fluids do not coat the relatively cool machine parts with a film of lubricant. This can lead to problems on machines that rely on the metalworking fluid for slideway or other mechanical lubrication. The incorporation of a small amount of emulsified oil to form a semichemical metalworking fluid is currently a popular solution to this problem. The adoption of a more rigorous machine lubrication program is also effective in some cases.

Since elevated temperatures are required for the polyalkylene glycol to come out of solution and coat the hot die surface, forming lubricants containing these polymers can have trouble during start-ups when the dies are cold. The problem is more severe when softer, nonferrous metals are being deformed. In these cases, unacceptable amounts of the softer workpiece material can transfer onto the die before operating temperatures have exceeded the cloud point of the polyalkylene glycol. These cold start-up problems can sometimes be overcome by initially increasing the concentration of the metalworking fluid to the point where it provides sufficient lubricity at ambient temperatures. Other possible solutions include the incorporation of a polymeric thickener or, alternative, emulsification of small amounts of mineral oil. Also being inves-

Copyright © 1999 Marcel Dekker, Inc.

tigated is the possibility of preheating the PAG-containing metalworking fluid during the startup.

## B. Laboratory Studies on Polyalkylene Glycols in Chemical Metalworking Fluids

There are many lubricity tests used to evaluate metalworking fluids in the laboratory. The pin and V-block, four-ball, and Timken wear tests are all commonly used. However, much better correlations with actual metalworking operations are obtained when fluids are evaluated under cutting or deformation conditions.

Three studies undertaken to examine the role of polyalkylene glycols in chemical metalworking fluids are presented in this section. The first utilized a plane strain compression test in which a lubricated aluminum coupon is plastically deformed. The remaining two studies used an instrumented lathe to evaluate different metalworking fluids while cutting a section of steel pipe. These studies provide strong evidence that supports the cloud point mechanism of polyalkylene glycol based chemical metalworking fluids described earlier in this chapter.

### 1. Plane Strain Compression Test: The Effect of PAG Cloud Point on the Performance of Chemical Metalworking Fluids

A plane strain compression press [49] was used to verify the cloud point mechanism of chemical metalworking fluids containing polyalkylene glycols. The press consists of two rectangular male dies, their faces measuring 0.25 in. × 1.5 in. The dies were attached to a 10-ton hydraulic press. Each die was equipped with thermostatically controlled heating elements so that the temperature surface could be controlled.

A one-inch-wide coupon made from a 0.16 cm thick sheet of 5252 aluminum, H28 temper, was thoroughly cleaned. A bead of lubricant was placed on each side of the coupon, which was then placed between the male dies of the plane strain compression press as shown in Fig. 7 [30]. The dies were forced together under a predetermined pressure that was great enough to cause plastic deformation of the coupon. The thickness of the coupon after deformation was measured, and the percent reduction was calculated using the following equation:

$$\%\ \text{reduction} = \left(1 - \frac{\text{final thickness}}{\text{initial thickness}}\right) \times 100\%$$

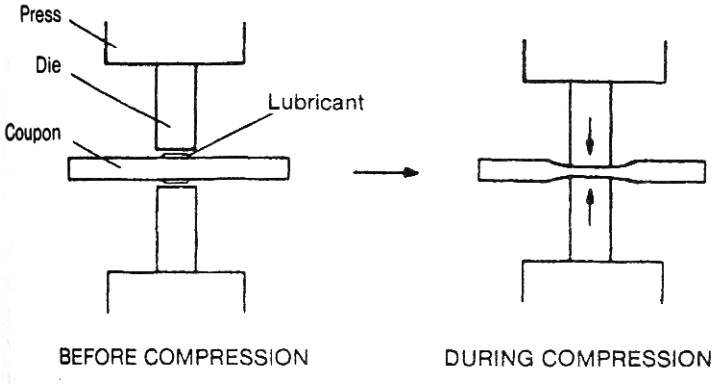



**Figure 7** The deformation of an aluminum coupon in a plane strain compression press. (From Ref. 30.)

Copyright © 1999 Marcel Dekker, Inc.

The greater the percent reduction, the better the lubricant.

Two chemical metalworking fluid concentrates, A and B, were made up using the formulation shown in Table 2. The only difference between concentrates A and B was the polyalkylene glycol used. The polyalkylene glycol used in concentrate A had a 1% cloud point of 37°C, while the polymer in concentrate B had an inverse solubility temperature of 65°C. Concentrates A and B were tested for lubricity using the plane strain compression press, as were 5% solutions of each in water. Fluid C, a kerosene-based aluminum cold rolling fluid, was also tested.

In this study a lubricated aluminum coupon was placed between the dies, which were brought together and held for 5 seconds at a pressure of 78,000 psi. The dies were then released and the percent reduction of the coupon determined. The lubricity of each fluid was tested at die temperatures ranging from 20 to 95°C. The results are plotted in Fig. 8 [30].

The effect of the cloud point of the polyalkylene glycol is evident from the results shown in Fig. 8. At all temperatures, concentrates A and B were excellent lubricants, giving percent reduction values of between 80 and 90%. This was to be expected, since the viscosities of concentrates A and B were quite high, 110 and 67 cSt at 40°C, respectively. The slight improvement of lubricity with increasing temperature may have been due to the evaporation of water from the concentrate, or to a mild cloud point effect.

At low temperatures, below the cloud point of either polymer, the lubricity of the 5% aqueous solutions of concentrates A and B was quite low. The percent reductions achieved using these dilute solutions of concentrates A and B were 50 and 45% respectively. Between 30 and 50°C, there was a sudden rise in the measured percent reductions of solution A, indicating a significant improvement in lubricity. This improvement in lubricity was centered around the cloud point of the product's polyalkylene glycol (37°C). Above 50°C, the 5% solution of fluid A provided lubricity equal to that of the concentrate.

The lubricity of the 5% solution of concentrate B showed the same behavior as the dilute concentrate A, only the increase in lubricity occurred between 60 and 75°C. As with the 5% solution of concentrate A, this improvement in lubricity bracketed the cloud point of the polyalkylene glycol used in concentrate B. Above 75°C, the dilute solution of fluid B provided the same lubricity as the concentrate.

The kerosene-based rolling lubricant showed poor lubricity at all temperatures, primarily because of its low viscosity of 4 cSt at 40°C. What is important is the decrease in its lubricity with increasing temperature, which occurs because the product's viscosity decreases as the temperature rises. While a more viscous hydrocarbon lubricant would provide much better lubricity, its performance would also be expected to decrease with increasing temperature owing to a drop in viscosity.

The results of this test support the cloud point mechanism of chemical metalworking fluids that contain polyalkylene glycols. It should be noted that this was a static test. In comparison to a high speed cutting operation, there was a relatively long time in this test for the polyalkylene glycol to come out of solution and form a lubricant film on the surfaces of the dies. However,

**Table 2** Metalworking Fluid Concentrate for Plain Strain Compression Study

| Component | Amount (wt %) |
|---|---|
| Polyalkylene glycol | 40 |
| Fatty acid | 10 |
| Ethanolamine | 20 |
| Water | 30 |

Copyright © 1999 Marcel Dekker, Inc.

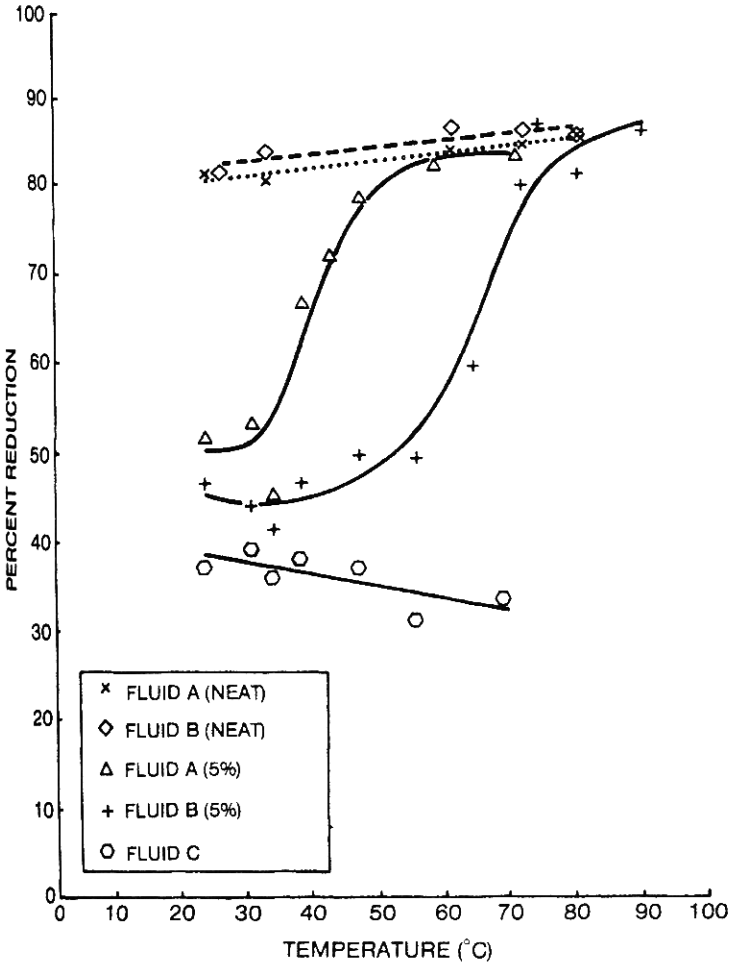



**Figure 8** Demonstration of the cloud point mechanism of chemical metalworking fluids containing polyalkylene glycols: data obtained from tests on a plane strain compression press. (From Ref. 30.)

while straight oil lubricity is not achieved in many cutting and forming operations, the improvement in performance due to the use of polyalkylene glycols in chemical metalworking fluids is well documented [6,24,30,48].

2. Lathe Test: The Effect of PAG Cloud Point on the Performance of Chemical Metalworking Fluids

A similar study was performed using a 16 in. Loge & Shipley single point turning lathe, instrumented with a strain gauge and a thermocouple. The thermocouple was inserted in the cutting tool. The tool holder was mounted on the strain gauge. A piece of 1026 steel pipe was end-cut while the metalworking fluid under evaluation was directed onto the rake face of the tool. The tool temperature and the vertical cutting force were monitored throughout the duration of the test Both cutting force [2,50,51] and tool temperature [2,5,13,52] have been shown to correlate with tool life. The lower the tool temperature and the cutting force, the more effective the metalworking fluid.

Copyright © 1999 Marcel Dekker, Inc.

**Table 3** Metalworking Fluid Concentrates for Cloud Point Study Using a Lathe

| | Component (%)[a] | | | | PAG properties | | |
|---|---|---|---|---|---|---|---|
| Sample | TEA | $H_2O$ | FA | PAG | Molecular Weight | Viscosity at 40°C (cSt) | Cloud point, 1% solution (°C) |
| A | 18 | 32 | 10 | 40 | 2700 | 400 | 37 |
| B | 18 | 32 | 10 | 40 | 2700 | 400 | 52 |
| C | 18 | 32 | 10 | 40 | 2700 | 400 | 100 |
| D | 18 | 32 | 10 | 40 | 2500 | 280 | >100 |
| E | 18 | 32 | 10 | 40 | 2000 | —[b] | >>100 |
| F | 18 | 72 | 10 | 0 | — | — | — |

[a] TEA, triethanolamine; FA, fatty acid.
[b] Product is a solid at room temperature due to high ethylene oxide content.

To show the effect of the inverse solubility of the polyalkylene glycol in a chemical metalworking fluid, five concentrates were made up differing only in the cloud point of the polyalkylene glycol used [53]. The concentrates tested are listed in Table 3. Each concentrate was diluted 20:1 with water and then tested under cutting conditions 1–5, with condition 5 being the most severe.

The results of this test are shown in Table 4. A good correlation exists between decreasing cloud point and enhanced performance. Fluids A and B, with cloud points of 37 and 52°C, respectively, cut effectively under all five conditions. Fluid C, which contains a polyalkylene glycol with a cloud point of approximately 95°C, failed under condition 5. Fluids D and E, whose cloud points were both greater than 100°C, failed at condition 4. Fluid F, which contained no polyalkylene glycol, failed at condition 3. The results of this work demonstrate the cloud point mechanism of chemical metalworking fluids in an actual metal removal operation.

3. Lathe Test: The Synergy Between PAGs and Fatty Acids, and PAGs and Phosphate Esters

The instrumented lathe was used to demonstrate the synergy that exists between polyalkylene glycols and polar, water-soluble lubricity additives [30]. Five concentrates were made up so that the sum of the polyalkylene glycol and the lubricity additive was equal to 40% by weight. The percentage of polymer ranged from 40 to 0, while the percentage of lubricity additive went

**Table 4** Lathe Test Results for Cloud Point Study[a]

| | Condition 1 | | Condition 2 | | Condition 3 | | Condition 4 | | Condition 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample | T | F | T | F | T | F | T | F | T | F |
| A | 94 | 490 | 100 | 540 | 104 | 550 | 114 | 610 | 122 | 680 |
| B | 92 | 500 | 100 | 540 | 104 | 570 | 116 | 640 | 126 | 710 |
| C | 100 | 500 | 102 | 540 | 108 | 540 | 108 | 640 | Failure | |
| D | 96 | 500 | 102 | 540 | 108 | 570 | Failure | | | |
| E | 96 | 510 | 106 | 540 | 102 | 580 | Failure | | | |
| F | 100 | 520 | 186 | 548 | Failure | | | | | |

[a] T, cutting tool temperature in degrees Celsius; F, vertical cutting force in pounds-force; Failure, either severe vibration or tool breakage.

Copyright © 1999 Marcel Dekker, Inc.

**Table 5** Metalworking Fluid Concentrates (%) Used in the Lathe Synergy Study

| PAG | Lubricity additive | TEA | Water |
|---|---|---|---|
| 40 | 0 | 40 | 20 |
| 30 | 10 | 40 | 20 |
| 20 | 20 | 40 | 20 |
| 10 | 30 | 40 | 20 |
| 0 | 40 | 40 | 20 |

from 0 to 40. The concentrates, shown in Table 5, were then diluted 20:1 with water and evaluated on the lathe.

Two different studies were run. In the first, the lubricity additive was a fatty acid. The results from this study are shown in Fig. 9. The minimum cutting force was achieved with polyalkylene glycol levels of between 20 and 30%. Maximum cooling, represented by the minimum tool temperature, occurred when the concentrate contained between 10 and 20% polymer. These curves show that combinations of the polyalkylene glycol and fatty acid perform better than either additive by itself.

In the second study, a water-soluble phosphate acid ester was employed as the EP lubricity additive. The data from this study are shown in Fig. 10. In this case, minimum cutting force was achieved with polyalkylene glycol levels of between 10 and 20% in the concentrate. The minimum tool temperature occurred between 0 and 30% polymer. Again, combinations of polyalkylene glycol and lubricity additive performed better than either additive used individually. This synergy further supports the cloud point mechanism of chemical metalworking fluids containing polyalkylene glycols.

## C. Modified PAGs in Chemical Metalworking Fluids

Polyalkylene glycols provide good lubricating properties in a large number of metalworking operations. They are also very stable in hard water, low foaming, and resistant to biological attack. When PAGs are used in combination with additives such as fatty acids or phosphate esters, the lubricating and cooling properties of the metalworking fluid are enhanced. Unfortunately, both fatty acids and phosphate esters are sensitive to hard water, prone to foaming, and susceptible to biodegradation. In an attempt to achieve the benefits of these combinations without the drawbacks, two types of modified polyalkylene glycol have been commercialized. These modified polyalkylene glycols are either esterified or grafted with organic acids.

Polyalkylene glycol esters are made from the condensation reaction between organic acids and the terminal hydroxyl groups of the alkoxylated polymer. These products like polyalkylene glycols, exhibit inverse solubility in water and thus behave in an analogous manner. Polyalkylene glycol esters exhibit good boundary lubricating properties [36,54], yet have better hard water stability and are less likely to foam than blends of fatty acids and unmodified polyalkylene glycols [22].

A second method of modifying polyalkylene glycols that has gained commercial acceptance is the addition of organic acid functionalities through grafting technology. The result is an anionic polyalkylene glycol that has organic acid groups randomly attached to the polymer's back-

Copyright © 1999 Marcel Dekker, Inc.

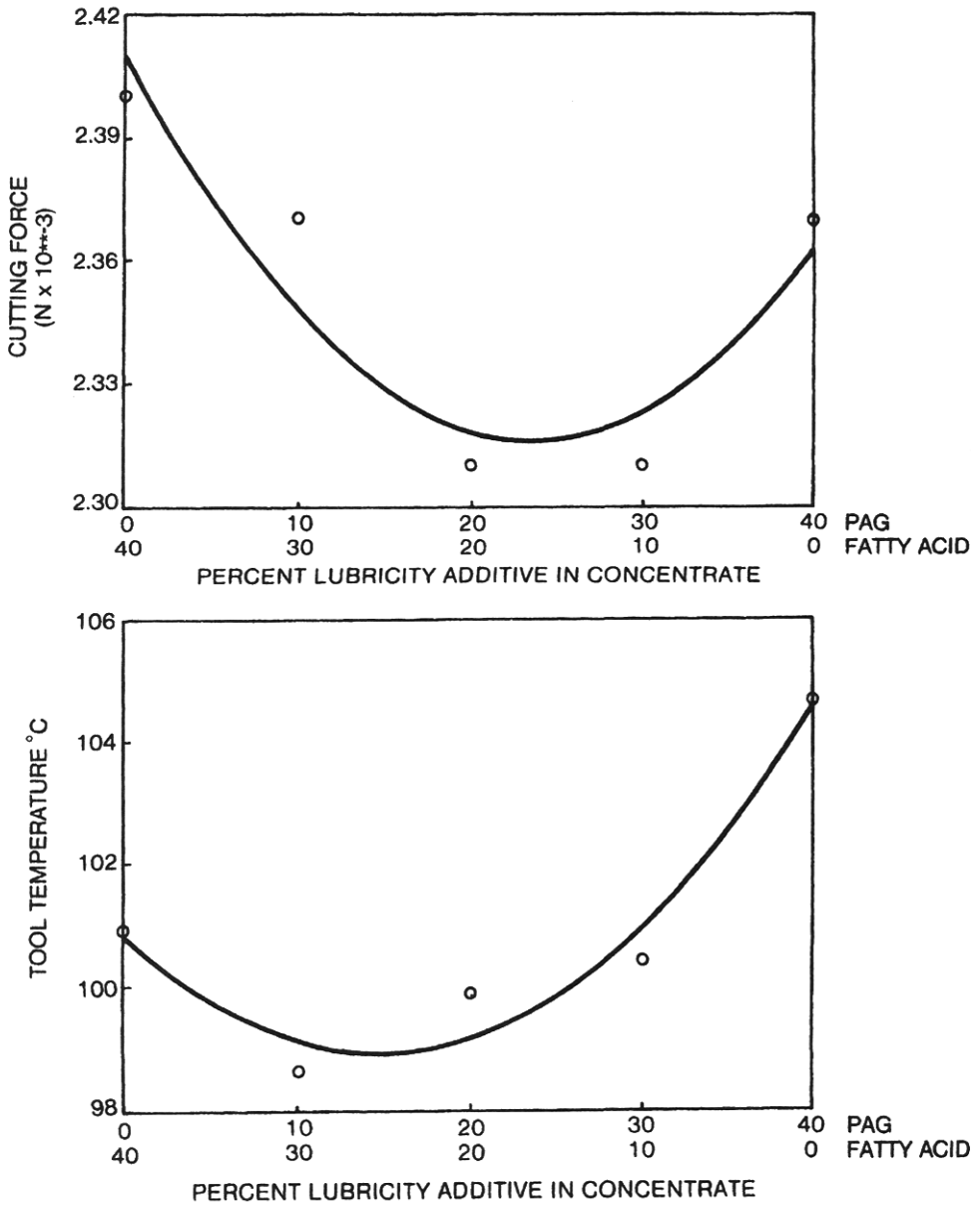



**Figure 9** Demonstration of the synergy between polyalkylene glycols and fatty acids in chemical metalworking fluids: data obtained from tests on an instrumented lathe. (From Ref. 30.)

bone with hydrolytically stable covalent bonds. These modified polyalkylene glycol polymers exhibit inverse solubility and excellent hydrodynamic and boundary lubricity. Because the acid groups are randomly attached to the polymer, the foaming tendencies of this type of product are significantly lower than those of blends of fatty acids and polyalkylene glycols. Since the polyalkylene glycol itself is very water soluble at room temperature, the grafted polymer has excellent hard water stability. Its resistance to biological attack is also very good [55].

Copyright © 1999 Marcel Dekker, Inc.

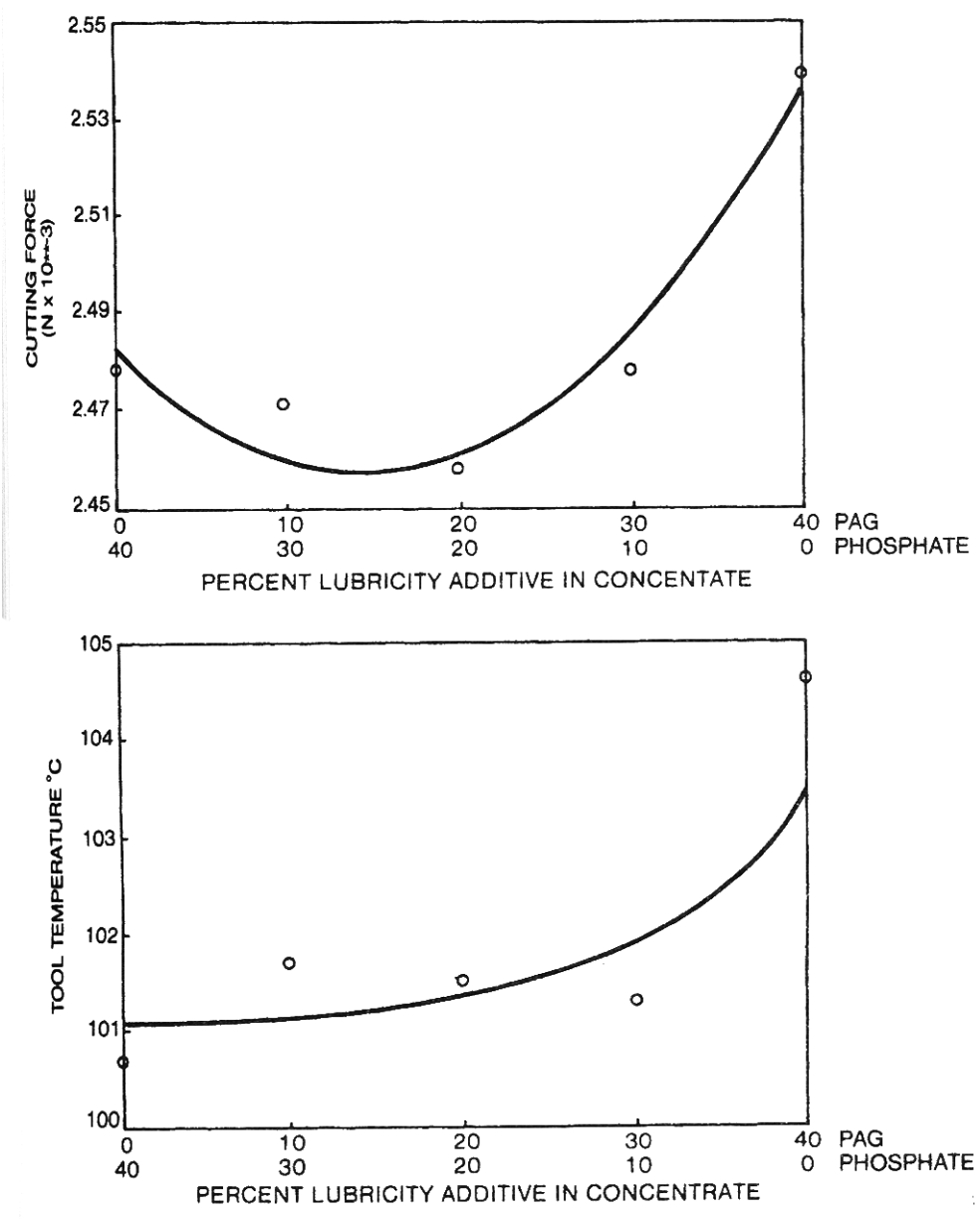



**Figure 10** Demonstration of the synergy between polyalkylene glycols and phosphate esters in chemical metalworking fluids: data obtained from tests on an instrumented lathe. (From Ref. 30.)

## D. Applications of PAGs in Chemical Metalworking Fluids

Polyalkylene glycols have been used in chemical metalworking fluids for the past 40 years. Because of their good lubricity and synergy with other water-soluble lubricity additives, they have helped expand the applications of chemical metalworking fluids.

Chemical metalworking fluids containing polyalkylene glycols have all the advantages char-

Copyright © 1999 Marcel Dekker, Inc.

acteristic of this product class. These advantages include excellent cooling, good biological and hard water stability, transparency, and cleanliness. The presence of the polyalkylene glycols in chemical metalworking fluids enables the formulation of products with enhanced lubricity properties, allowing them to compete directly with heavy-duty soluble oils in many applications.

While polyalkylene glycols or modified versions have been used in chemical metalworking fluids for many years [19,24,37], performance data comparing these products to metalworking fluids of other types are relatively scarce. Articles comparing different classes of metalworking fluids to each other (e.g.) chemical solutions vs. soluble oils, soluble oils vs. straight oils) are readily found in the literature. However, the specific formulation information needed to examine the effects of synthetic lubricants in these products is rarely included. The rest of this section reviews some of the documented work that demonstrates the effect of polyalkylene glycols, both normal and modified, in chemical metalworking fluids. The use of polyalkylene glycol based metalworking fluids in grinding, tapping, hobbing, rolling, drawing, and forming operations is described.

1. Grinding

Levesque et al. published a paper in 1984 describing their experience with an acid-grafted polyalkylene glycol in three different grinding operations [55].

In the first case a mineral seal oil fortified with approximately 5% of a fatty acid was used to grind hardened steel balls. Odor, general housekeeping problems, and a concern about the flammability of the oil caused the investigators to switch to a water-based metalworking fluid.

A chemical metalworking fluid based on a mixture of caprylic acid and a polyalkylene glycol was selected for the ball grinding operation. Initially the product worked very well. During use, however, the effectiveness of this fluid gradually decreased. The addition of concentrate was necessary to return the coolant to acceptable performance levels. Analytical testing of the coolant during use showed that the drop in performance was due to the selective depletion or biodegradation of the caprylic acid. Rather than continually monitor their fluid for acid concentration, the authors switched to a dilute solution of an amine-neutralized, acid-grafted polyalkylene glycol. This modified polyalkylene glycol performed well.

The second case study involved a centerless roller grinding operation. A heavily fortified soluble oil was used in a 7000-gallon central sump. The soluble oil, however, covered the regulatory wheels with a layer of oil and metal fines, which prevented the achievement of the desired tolerances. The authors decided to switch to a chemical metalworking fluid because of cleanliness of this type of product.

The soluble oil was replaced with a chemical metalworking fluid containing a fatty acid ester, a boric acid corrosion inhibitor, and a biocide. Initially the product worked well, but within a month the surface finishes had degraded to an unacceptable level. The depletion of the fatty ester was determined to be the problem.

The authors then switched to the amine-neutralized, acid-grafted polyalkylene glycol fortified with a carboxylic acid based corrosion inhibitor. At the time the paper was written, the roller grinding operation had been using this chemical metalworking fluid for 16 months with essentially no problems due to depletion or biodegradation.

In the third study conducted by the authors, the same chemical metalworking fluid based on the acid-grafted polyalkylene glycol was used in a double-disk surface grinding operation. The life of this coolant system was more than 8 months, compared with only 2–3 months with the soluble oil used initially.

Copyright © 1999 Marcel Dekker, Inc.

2. Tapping

In 1985 Nash and Colakovic published a study on the effect of a polyalkylene glycol ester and three other lubricity additives on the performance of chemical metalworking fluids during the tapping of high silicone content aluminum blanks [54].

The fluids were evaluated using a tapping torque test machine [56]. The taps employed were HSS, 3-flute, 10–15 mm. The tap surface speed was 0.508 m/s. The nut blanks were made from high silicone A380.1 aluminum with a 16–25 rms non-heat-treated surface finish.

The chemical metalworking fluids were diluted to 10% of their original concentration with 140 ppm hardness water. The torque required to tap the nut blanks was recorded and compared to that achieved when a straight oil metalworking fluid was used. This control oil was a neat cutting fluid fortified with chlorine-and sulfur-containing lubricity additives. The percent tapping efficiency was then calculated using the following equation:

$$\% \text{ efficiency} = \frac{\text{control oil torque}}{\text{test fluid torque}} \times 100\%$$

The higher the percent tapping efficiency, the better the metalworking fluid.

A series of chemical metalworking fluids was made up to determine the effects on tapping efficiency of four water-soluble lubricity additives: a polyalkylene glycol ester that exhibits inverse solubility, an alkyl acid phosphate, a sulfurized oleic acid, and a chlorinated oleic acid. Each fluid also contained a carboxylate salt for corrosion protection and triethanolamine to solubilize the lubricity additives and provide reserve alkalinity. The physical characteristics of the components used to make up the test concentrates are shown in Table 6.

The compositions of the different fluids tested and their average percent tapping efficiency are shown in Table 7. These data indicate that the largest positive effects of a single component come from the addition of the polyalkylene glycol ester or the alkyl acid phosphate. Furthermore, the combination of the PAG ester and phosphate was synergistic, providing lower tapping torques and thus better efficiency than the sulfurized, chlorinated reference oil. The addition of the sulfurized oleic acid resulted in a small improvement over the base formulation and also showed synergy when combined with the polyalkylene glycol ester. The use of the chlorinated oleic acid had no significant effect on tapping efficiency.

3. Hobbing

Katsuki et al. described work that they had done to evaluate the performance of water-based metalworking fluids in a gear hobbing operation [57]. In this study the durability of the hob

**Table 6** Physical Characteristics of Fluid Components

| Component | Kinematic Viscosity (cSt) | | Total acid number | Miscellaneous properties |
|---|---|---|---|---|
| | At 40°C | At 100°C | | |
| Water | — | — | — | 140 ppm hardness |
| Carboxylate salt | 300 | — | 170 | 140 base number |
| TEA | 222 | 14 | — | |
| PAG ester | 2750 | 230 | 15 | 1% cloud point, 77°C |
| Alkyl acid phosphate | 95 | 18 | 330 | 11% phosphorus |
| Sulfurized oleic acid | 190 | 20 | 185 | 8.5% sulfur |
| Chlorinated oleic acid | 150 | 22 | 140 | 30% chlorine |

Copyright © 1999 Marcel Dekker, Inc.

**Table 7** Test Fluid Concentrate Compositions and Aluminum Tapping Torque Efficiency

| | Solution concentrates | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Component | Base | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| Water | 84 | 74 | 80 | 70 | 80 | 70 | 76 | 66 | 80 | 70 | 76 | 66 | 76 | 66 | 72 | 62 |
| Carboxylate salt | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| TEA | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 | 8 |
| PAG ester | — | 10 | — | 10 | — | 10 | — | 10 | — | 10 | — | 10 | — | 10 | — | 10 |
| Phosphate | — | — | 4 | 4 | — | — | 4 | 4 | — | — | 4 | 4 | — | — | 4 | 4 |
| Sulfurized acid | — | — | — | — | 4 | 4 | 4 | 4 | — | — | — | — | 4 | 4 | 4 | 4 |
| Chlorinated acid | — | — | — | — | — | — | — | — | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| % Efficiency, mean value | 79 | 91 | 90 | 101 | 84 | 97 | 92 | 101 | 80 | 81 | 97 | 99 | 88 | 91 | 84 | 91 |



Copyright © 1999 Marcel Dekker, Inc.

**Table 8** Polyalkylene Glycols Evaluated in Hobbing Study

| Sample | MW | Viscosity at 30°C (cSt) | VI | Diluted viscosity at 40°C (cSt) |
|---|---|---|---|---|
| PAG-1 | 1,675 | 205 | 203 | 1.29 |
| PAG-2 | 2,430 | 276 | 210 | 1.41 |
| PAG-3 | 4,750 | 1,590 | 290 | 2.16 |
| PAG-4 | 11,800 | 27,500 | 427 | 5.26 |

was evaluated using a fly-tool cutting test on a milling machine. This fly-tool cutting evaluation was set up to correlate closely with an actual gear hobbing operation.

The metalworking fluid concentrates were diluted with water. During the cutting operation, the face of the hob was flooded with the diluted metalworking fluid. Grooves were cut into the workpiece to correspond to the manufacture of 14.7 gears. The hob was then evaluated for corner and center wear. The smaller the wear scars, the more effective the metalworking fluid.

Four water-soluble polyalkylene glycols of different molecular weights were evaluated and compared to a chlorinated fatty oil that was considered an excellent gear cutting lubricant. The polyalkylene glycols were all diluted 10 times with water and then compared to the oil-based standard. The polyalkylene glycols evaluated are characterized in Table 8. The results are shown in Table 9.

The data in Table 9 show that the center wear of the chlorinated fatty oil control was lower than that of any of the polyalkylene glycols. The differences were more extreme at the intermediate cutting speeds of 86 and 117 m/min. At these intermediate speeds, increasing the molecular weight of the polyalkylene glycol tends to decrease the center wear. However, at cutting speeds of 62 and 159 m/min, essentially no difference was seen between the performance of the different molecular weight polymers.

The corner wear experienced when the polyalkylene glycols were used was equivalent to that of the chlorinated fatty oil at a cutting speed of 62 m/min. As cutting speed increased, however, the corner wear seen when the oil-based control was used rose much more quickly than with the polyalkylene glycols. There was no significant affect of polyalkylene glycol molecular weight on corner wear.

A second study was performed to determine the effect of polyalkylene glycol concentration on hobbing performance. Polymer PAG-4 was tested over a wide range of dilutions and compared to water and the chlorinated fatty oil control at a cutting speed of 159 m/min. The results are shown in Table 10.

This study demonstrates that even at very low concentrations, the presence of the polyalkylene glycol yields very low corner wear relative to water. At concentrations equal to or greater

**Table 9** Results from Hobbing Evaluation

| Cutting speed (m/min) | Center wear (mm) | | | | | Corner wear (mm) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Control | PAG-1 | PAG-2 | PAG-3 | PAG-4 | Control | PAG-1 | PAG-2 | PAG-3 | PAG-4 |
| 62 | 0.07 | 0.11 | 0.12 | 0.11 | 0.12 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| 86 | 0.10 | 0.28 | 0.22 | 0.16 | 0.18 | 0.17 | 0.11 | 0.11 | 0.11 | 0.11 |
| 117 | 0.14 | 0.48 | 0.50 | 0.37 | 0.29 | 0.27 | 0.12 | 0.12 | 0.12 | 0.15 |
| 159 | 0.18 | 0.21 | 0.20 | 0.20 | 0.20 | 0.50 | 0.16 | 0.16 | 0.16 | 0.15 |

Copyright © 1999 Marcel Dekker, Inc.

**Table 10** Effect of Polyalkylene Dilution Ratio on Hobbing Performance

| PAG-4 concentration (%) | Center wear (mm) | | | Corner wear (mm) | | |
|---|---|---|---|---|---|---|
| | PAG-4 | Water | Control oil | PAG-4 | Water | Control oil |
| 0.10 | 0.11 | 0.11 | 0.18 | 0.60 | 1.02 | 0.50 |
| 0.20 | 0.11 | | | 0.48 | | |
| 0.33 | 0.12 | | | 0.60 | | |
| 0.62 | 0.16 | | | 0.22 | | |
| 1.25 | 0.17 | | | 0.21 | | |
| 2.50 | 0.18 | | | 0.20 | | |
| 5.00 | 0.16 | | | 0.11 | | |
| 10.00 | 0.20 | | | 0.11 | | |

than 0.62%, the use of the PAG-4 solution also results in lower corner wear than occurred with the chlorinated fatty oil control, and equivalent center wear. It is interesting to note that while corner wear decreased with increasing polyalkylene glycol concentration, center wear increased.

The authors of this study found that while the use of the polyalkylene glycols provided superior performance as measured by lower wear, the corrosion protection provided by these test solutions was insufficient. It was found that the addition of rust preventives could significantly improve the corrosion protection provided by the polyalkylene glycol. However, the addition of these corrosion inhibitors cause hob wear to increase at higher cutting speeds.

4. Machining and Rolling

A number of chemical metalworking fluid formulations based on polyalkylene glycols and mixtures of these polymers with polyvinylpyrrolidone, polyvinyl alcohol, polyacrylates, and polymethacrylates were patented by Marx [47]. Several of these formulations and their applications are shown in Table 11. The formulations in this table were used successfully in a number of machining and sheet rolling operations.

Marx also described how the replacement of soluble oils with chemical metalworking fluids containing the aforementioned water-soluble polymers enabled cutting speeds to be increased in a number of sawing, planing, and drilling applications. These metalworking fluids were also successful at replacing straight oils in deep hole drilling operations, a result that yielded significant cost savings.

Marx also described how aqueous solutions containing 15–20% polyalkylene glycol or mixtures of polyalkylene glycols and some of the higher molecular weight polymers mentioned earlier can be used for deep drawing steel and stainless steel parts. These solutions can also be used for the drawing of wire and tubing. These polymers can be used to advantage in drawing operations because residues are easily washed off with water.

5. Blanking and Drawing

The early use of polyalkylene glycol solutions in blanking and drawing operations was documented by Sweatt and Langer in 1951 [37]. The properties of the polyalkylene glycol used in these chemical metalworking fluids are shown in Table 12.

A 25% solution of this polyalkylene glycol in water with a small amount of corrosion inhibitor was used to replace a petroleum oil based lubricant in a blanking and a drawing operation. The two applications are summarized in Table 13. While the good lubricity of the polyalky-

Copyright © 1999 Marcel Dekker, Inc.

**Table 11** Formulations and Applications of Chemical Metalworking Fluids Containing Polyalkylene Glycols

| | Concentrate formulation (%) | | | |
|---|---|---|---|---|
| Component | Fluid 1 | Fluid 2 | Fluid 3 | Fluid 4 |
| PAG | 20 | 15 | 15 | 20 |
| Polyvinylpyrrolidone | — | 5 | 5 | — |
| Polyvinyl alcohol | — | — | — | 4 |
| Amine phosphate | — | — | — | — |
| CI[a] | — | — | 46 | 46 |
| TEA | 6 | 6 | — | — |
| Water | 74 | 74 | 24 | 30 |
| Dilution ratio | 20:1 | 20:1 | 20:1 | 10:1 |
| Application | Steel sheet rolling; brass and copper sheet formation | Rolling of thin foils (Cu, Sn, Au, brass) | Steel tapping; rod and channel formation | Steel planing, milling, and cutting |

[a] Corrosion inhibitor package containing 16 parts of benzoic acid, 9 parts of TEA (triethanolamine), 15 parts of triethanolamine phosphate, and 6 parts of morpholine.

**Table 12** Polyalkylene Glycol Characteristics

| Property | Value |
|---|---|
| Molecular weight | 1600 |
| Viscosity, cSt | |
| At 40°C | 132 |
| At 100°C | 26 |
| Specific gravity, 20/20°C | 1.05 |
| Water solubility at 25°C | Complete |
| 1% Cloud point, °C[a] | 50 |

[a] Inverse solubility temperature.

**Table 13** Applications of Aqueous Polyalkylene Glycol Solutions

| Operation | Workpiece material | Metalworking fluid | Number of pieces per die refinishing |
|---|---|---|---|
| Blanking and pressing | Annealed spring steel | Oil | 35,000–50,000 |
| | | PAG solution[a] | 100,000–120,000 |
| Drawing shells | Nickel-plated steel | Oil | 25,000–30,000 |
| | | PAG solution[a] | >65,000 |

[a] Solutions contained 25% polyalkylene glycol.

Copyright © 1999 Marcel Dekker, Inc.

**Table 14** Cold-Forming Lubricant Formulation

| Component | Amount (vol %) | Component description |
|---|---|---|
| Polyalkylene glycol | 32 | Molecular weight, 2200<br>40 wt % ethylene oxide (EO)<br>60 wt % propylene oxide (PO) |
| Sulfurized fatty acid | 5 | 14 wt % sulfur |
| Chlorinated fatty acid | 5 | 35 wt % chlorine |
| Glycerin | 3 | |
| Potassium nitrite | 2 | |
| Potassium hydroxide | 1.75 | |
| Silicone defoamer | 0.10 | |
| Water | 51.15 | |

lene glycols is evident from the increased tool life, their cleanliness and water washability also are important.

6. Cold Forming

A chemical metalworking fluid formulation for use in cold forging operations was patented by Felton [48]. The formulation is shown in Table 14. This metalworking fluid was used neat to successfully form 0.75 in. hexagonal nut blanks from 0.75 in. rod of AISI 1038 steel. The nuts were formed at a rate of 2 blanks each second in a five-step operation. The die used in each step was flooded with lubricant between hits. The trial was run without problems for 5 hours, indicating good lubrication.

The finished blanks were bright and shiny when the polyalkylene glycol based metalworking fluid was used, as opposed to the dull, scorched appearance that resulted when a straight oil forming lubricant was employed. Also, the smoke generated during this operation was greatly reduced when the forming lubricant was switched from the oil to the polyalkylene glycol based product.

7. Drawing and Forming

The use of a polyalkylene glycol based chemical metalworking fluid in a number of drawing and forming operations was described by Brown [58]. The formulation (Table 15) was used at various dilutions with water, depending on the severity of the operation. Up to 5% of a sulfurized fatty acid was added for additional extreme pressure lubrication when needed.

**Table 15** Polyalkylene Glycol Based Drawing and Forming Lubricant

| Component | Amount (wt %) |
|---|---|
| Polyalkylene glycol | 15 |
| Phosphate acid ester | 6 |
| Corrosion inhibitor (nonnitrite) | 15 |
| Triethanolamine | 10 |
| Sulfurized fatty acid | 0–5 |
| Water | 49–54 |

Copyright © 1999 Marcel Dekker, Inc.

The operations in which this formulation was used are summarized in Table 16. The first three operations are described in more detail in the following sections.

*Trailer Hitches.* Trailer hitches were being drawn from HRPO AKDQ C 10–08 (0.141–0.151 in. thick) drawing quality steel using an 800-ton press. Ten hitches were drawn each minute. When a straight oil metalworking lubricant fortified with a chlorinated paraffin was used, the dies had to be refinished every 15,000–20,000 parts. While the lubricity provided by the chlorinated oil was good, it was very difficult to completely remove the lubricant from the formed pieces. Also, the operators complained of skin irritation while using the chlorinated product.

The straight oil was therefore replaced by the polyalkylene glycol based metalworking fluid shown in Table 15. This formulation was fortified with 5% of the sulfurized fatty acid and used without further dilution with water. Die life remained unchanged at 15,000–20,000 hitches per refinishing. However, the polyalkylene glycol based lubricant provided excellent corrosion protection while the formed parts were stored and could be easily removed with aqueous cleaning systems prior to subsequent operations. More importantly, the operators found the product to be benign.

*Water Heater Tops and Bottoms.* A soluble oil metalworking fluid formulated with rust inhibitors and diluted 20 times with water was being used to form water heater tops and bottoms. The operation involved a 4 in. draw of 9–10 gauge mild cold-rolled steel. The pieces were produced at a rate of 10 per minute. However, the soluble oil was very difficult to completely remove from the formed pieces. The presence of residual oil caused defects in the enamel coating, which in turn led to the premature corrosion of the water heater.

The soluble oil was replaced with the chemical metalworking fluid shown in Table 15, diluted 20:1 with water and used without the sulfurized fatty acid. The polyalkylene glycol based metalworking fluid provided lubricity equivalent to that from the soluble oil. More importantly, this chemical metalworking fluid was easily washed from the formed parts, virtually eliminating defects in the enamel coatings.

**Table 16** Applications of Polyalkylene Glycol Based Forming Lubricant

| Application | Process description | PAG/fluid dilution ratio, $H_2O$:lube | Previous product[a] | Observations |
|---|---|---|---|---|
| Trailer hitches | Severe draw | Neat | Chlorinated paraffin | Nonstaining, Nonirritating; good die life |
| Water heater tops and bottoms | Blanking and one 2 in. draw | 20:1 | R&O sol oil (dil 20:1) | Water washable; good rust protection |
| Water heater jacket tops | Cone spinning, 40% elongation | 20:1 | Chlorinated sol oil (dil 10–20:1) | Good cooling and lubrication |
| Oven liners | Five-stage operation (four 0.5 in. draw, one shear/punch) | 2:1 | Chlorinated sol oil (dil 2:1) | Water washable; no staining |
| Lawnmower bodies | Blanking operation and one 4 in. draw | 2:1 | Chlorinated sol oil (dil 2:1) | Excellent rust protection; good die life |

[a] Rust and oxidation inhibited soluble oil metalworking fluid.

Copyright © 1999 Marcel Dekker, Inc.

*Cone Spinning of Water Heater Jacket Tops.* Tops for water heater jackets were made in a cone spinning operation. A 16 in. diameter disk made from mild cold-rolled steel was blanked in a separate step. During the cone spinning operation, this disk was spun at 1500–1700 rpm and made to undergo a 40% elongation. The wheel of the cone spinning machine was flooded with a 20:1 dilution of a chlorinated soluble oil. This metalworking fluid provided insufficient cooling and lubricity, which resulted in the discoloration of the workpiece.

The chlorinated soluble oil was replaced with the chemical metalworking fluid shown in Table 15 fortified with the sulfurized fatty acid. This product was also used as a 5% solution in water. The lubricity and cooling properties of this product were excellent. Also, this chemical metalworking fluid provided the spun workpiece with corrosion protection during storage for more than 60 days.

8. Summary of PAG Applications in Chemical Metalworking Fluids

Polyalkylene glycol fortified chemical metalworking fluids are effective coolants and lubricants in a wide range of metal removal and deformation operations. They have replaced both soluble oils and straight oil metalworking fluids. The polyalkylene glycol containing products have all the beneficial properties of chemical metalworking fluids, including excellent cooling, ease of maintenance, and cleanliness. In addition, they exhibit enhanced lubricity that enables them to compete with heavy-duty soluble oils and, in some cases, straight oil metalworking fluids. The properties of polyalkylene-based chemical metalworking fluids make them especially desirable in applications in which water solubility is important or workpiece staining must be avoided.

## VI. SYNTHETIC LUBRICANTS IN SEMICHEMICAL METALWORKING FLUIDS

As the name implies, semichemical metalworking fluids are a hybrid of soluble oils and chemical solutions. Their main advantage is that they are cleaner and better coolants than soluble oils but still contain emulsified hydrocarbons, which provide good corrosion protection and lubricity to both the tool or die and the machinery.

A typical formulation for a semichemical metalworking fluid concentrate is shown in Table 17. This concentrate will be diluted 20:1 to 40:1 with water for most cutting or grinding operations. For more severe metalworking operations, higher concentrations are employed.

Synthetic lubricants in semichemical metalworking fluids are used primarily as water-soluble lubricity additives. Canter et al. [36] described the use of polyalkylene glycol esters in

**Table 17** Typical Semichemical Concentrate Formulation

| Component | Amount (wt %) |
|---|---|
| Mineral oil | 5–20 |
| Emulsifiers | 5–20 |
| Couplers | 0–5 |
| Corrosion inhibitors | 5–10 |
| EP additives | 0–10 |
| Water-soluble lubricity additives | 0–20 |
| Biocides | —[a] |
| Water | 40–70 |

[a] As recommended by the manufacturer.

Copyright © 1999 Marcel Dekker, Inc.

**Table 18** Semichemical Test and Reference Formulations

| Component | Test formulation (% component) | Reference fluid (% component) |
|---|---|---|
| Naphthenic oil | 3–13 | 8 |
| Emulsifier base | 9–20 | 12 |
| PAG ester | 10 | — |
| Amine borate | 6 | 6 |
| Triazine | 2 | 2 |
| Propylene glycol methyl ether | 1.5 | 1.5 |
| Water | 60.5 | 70.5 |

semichemical metalworking fluid formulations. A number of esters were made up by reacting polyalkylene glycols with either 1 or 2 equiv of a fatty methyl ester. The polyalkylene glycols used had ethylene oxide/propylene oxide ratios of 5:1, 3:1, and 1:1. The fatty groups evaluated were pelargonate, laurate, oleate, and stearate. Many of these compounds displayed inverse solubility properties in water.

The polyalkylene glycol esters were incorporated into the base formulation shown in Table 18. The oil-to-emulsifier base ratios were adjusted to enable the formation of a stable microemulsion for each polyalkylene glycol ester tested. The reference semichemical fluid formulation is also shown in Table 18.

All the semichemical metalworking fluid formulations containing polyalkylene glycol esters provided significantly better lubricity than the reference fluid at the same concentration on a pin and V-block wear test at a 10:1 dilution with water. Two of the formulations containing dioleate esters as well as the product made with the dipelargonate ester were also low foaming and provided better corrosion protection than the reference fluid.

Another growing use for polyalkylene glycols in semichemical metalworking fluids is as coupling agents to help solubilize the corrosion inhibitor packages [34].

In theory, synthetic hydrocarbons like poly(α-olefins) could be used in place of the emulsified mineral oil in a semichemical formulation. The cost of this substitution usually outweighs the benefits in most applications. In a small number of cases, however, such formulations are marketed for use in operations where no mineral oils are allowed yet an emulsified lubricant phase is desired.

## VII. SYNTHETIC LUBRICANTS IN SOLUBLE OIL METALWORKING FLUIDS

Soluble oil metalworking fluids still make up a majority of the water-based lubricants used today. They are well accepted, and the presence of a hydrocarbon oil provides many operators and machinists with a significant degree of comfort. A typical soluble oil concentrate formulation is shown in Table 19.

The use of synthetic lubricants in soluble oil metalworking fluids is very small. Water-soluble synthetic lubricants are not used in soluble oil formulations. Synthetic hydrocarbons or esters could be emulsified along with or in place of the mineral oil, but the cost of such substitutions usually outweighs the benefits. However, as with semichemical metalworking fluids, there are specialty applications in which synthetic hydrocarbons are emulsified to make "synthetic" soluble oils. This is usually done to satisfy customers who require oil-free metalworking fluids

Copyright © 1999 Marcel Dekker, Inc.

**Table 19** Typical Soluble Oil Concentrate Formulation

| Component | Amount (wt %) |
|---|---|
| Mineral oil | 70–85 |
| Emulsifiers | 10–20 |
| Coupling agents | 1–5 |
| Corrosion inhibitors | 5–10 |
| EP additives | 0–10 |
| Biocide | —[a] |
| Water | 0–5 |

[a] As recommended by the manufacturer.

but need an emulsified product. Such formulations can also be used in applications where the workpiece is susceptible to staining.

Another application for synthetic lubricants is in rolling oils for steel. These products are usually soluble oils containing mineral oils and tallow fats. These natural fats are being replaced in some cases by synthetic esters made from the reaction between pentaerythritol or trimethylolpropane and $C_{12}$ to $C_{18}$ fatty acids [34].

Double-comb polymeric esters, made by reacting butanol with α-olefin dicarboxylic acid copolymers [39], have been used to formulate high performance soluble oil metalworking fluids. Several concentrates were made up to determine the effectiveness of the double-comb polymeric esters as lubricity additives. The concentrates were diluted with water to give 10% solutions and then evaluated using a Reichert frictional wear tester, which is believed to correlate well with a number of metalworking operations [39]. The results of this work are shown in Table 20. The addition of the double-comb polymeric ester greatly improves the performance of soluble oil formulations containing a variety of traditional phosphorus- and sulfur-containing extreme pressure lubricity additives.

The development of lubricity additives that can replace chlorinated and sulfurized compounds is a goal of the metal working industry. The elimination of chlorine is becoming increasingly desirable as the disposal of halogenated wastes becomes more difficult and costly. Sulfurized additives can promote microbial growth in the active metalworking fluid. Complex

**Table 20** Lubricity of Soluble Oils Containing Complex Polymeric Ester

| | Formulation | | | | | |
|---|---|---|---|---|---|---|
| Component | A | B | C | D | E | F |
| Double-comb polymeric ester, 357 cSt at 100°C | — | 10 | — | 10 | — | 10 |
| Mineral oil, 150 N | 75 | 65 | 70 | 60 | 72 | 62 |
| Emulsifier[a] | 25 | 25 | 25 | 25 | 25 | 25 |
| Dibutyl phosphite | — | — | 3 | 3 | — | — |
| Sulfurized fat, 16% sulfur | — | — | 2 | 2 | — | — |
| TPPT[b] | — | — | — | — | 3 | 3 |
| Reichert Test results, % relative abrasion[c] | 97 | 94 | 91 | 56 | 96 | 73 |

[a] Alkylbenzenesulfonate, soap, fatty acid alkanolamide.
[b] Triphenylphosphorothionate.
[c] Deionized water = 100% abrasion.

Copyright © 1999 Marcel Dekker, Inc.

**Table 21** Lubricity of Soluble Oils Containing Complex Polymeric Ester

| | Formulation | | | | |
|---|---|---|---|---|---|
| Components | Control | A | B | C | D |
| Soluble base | 21 | 15 | 15 | 15 | 15 |
| Complex polymeric ester | — | 5 | 2 | 3.5 | — |
| Amine phosphate | — | — | — | 0.5 | — |
| Triethanolamine | — | 0.75 | 0.30 | 0.90 | — |
| Sulfurized fat (10% inactive sulfur) | 10 | — | — | — | — |
| Chlorinated paraffin (60% chlorine) | 4 | — | — | — | — |
| Pale oil, 100 SUS | 65 | 79 | 83 | 79 | 85 |
| Tapping torque test, % efficiency | 100 | 106 | 96.8 | 100 | 93.5 |

polymeric esters based on pentaerythritol have been used in soluble oil formulations as lubricity additives to enable the replacement of chlorine and inactive sulfur in some applications [38].

Several soluble oil concentrates were blended using the complex polymeric ester in place of a sulfurized fat and a chlorinated paraffin that were used in the control formulation. All the products were then diluted with distilled water to form 5% solutions by weight. The diluted soluble oil metalworking fluids were evaluated by means of the tapping torque test, ASTM D-5619. High speed taps and 1215 steel nuts at 400 rpm were used in the evaluations. The control sample containing the chlorinated and sulfurized compounds was assumed to have a tapping efficiency of 100%. Higher tapping efficiencies mean better performance. Formulations A and C performed as well as or better than the control sample. The soluble oil formulations and tapping torque test results are shown in Table 21 [38].

## VIII. SYNTHETIC LUBRICANTS IN STRAIGHT OIL METALWORKING FLUIDS

Straight oil metalworking lubricants continue to be the products of choice in a large number of metalworking operations, particularly those involving drawing and forming or low speed, high severity metal removal. A typical straight oil formulation is shown in Table 22.

Straight oil metalworking fluids can be formulated with synthetic lubricants instead of mineral oils. The predominant synthetic lubricants used in straight oil metalworking fluids are polyalkylene glycols, polyisobutylenes, and esters. The major advantages of these products are low staining and clean burn-off characteristics. Several applications of straight oil metalworking fluids based on synthetic lubricants are described below.

**Table 22** Typical Formulation of a Straight Oil Metalworking Fluid

| Component | Amount (wt %) |
|---|---|
| Mineral oil | 75–100 |
| Corrosion inhibitors | 0–5 |
| EP additives | 5–20 |
| Boundary lubricity additives | 0–10 |
| Antioxidants | 0–2 |

Copyright © 1999 Marcel Dekker, Inc.

**Table 23** Applications of Neat Polyalkylene Glycols as Forming Lubricants

| Operation | Workpiece material | Metalworking lubricant | Number of pieces per die refinishing |
|---|---|---|---|
| Drawing | 85-15 Brass | Oil | 5,000 |
| | | PAG[a] | 17,000 |
| Drawing | Sheet iron | Oil | 50 |
| | | PAG[b] | 250 |

[a] Oil soluble; viscosity at 40°C, 27 cSt.
[b] Water soluble; viscosity at 40°C, 130 cSt.

The use of neat polyalkylene glycols in two drawing operations is described by Sweatt and Langer [37]. Their work is summarized in Table 23. In both operations die life was significantly increased by switching from an oil-based product to a polyalkylene glycol. When using an oil-soluble polyalkylene glycol to draw 85–15 brass, these authors also found that there was a significant reduction in tarnish. More importantly, it was possible to solder the brass pieces after drawing without first having to remove the lubricant. The use of a water-soluble polyalkylene glycol to draw sheet iron not only increased die life by a factor of 5 but also enabled the parts to be thoroughly cleaned using a water wash.

Similar observations were noted by Russ (1951, private communication, Union Carbide Corp.) while making 3 in. bubble caps. The caps were made from 0.064 in. thick copper sheet. The operation involved a 2.5 in. draw of the copper blanks. The original lubricant was lard oil. The use of the lard oil led to sticking between the die and the workpiece and discoloration of the finished caps. The lard oil was replaced by a water-soluble polyalkylene glycol having a viscosity of 80 cSt at 40°C. The use of this synthetic lubricant eliminated workpiece sticking and discoloration and also improved the surface finish of the drawn caps.

The addition of oil-soluble polyalkylene glycols to aluminum sheet and foil rolling lubricants has also been explored. Whetzel et al. [31] described how the addition of polyalkylene glycols to light mineral oils resulted in an increase in fluid performance. The percent reduction in thickness achieved when rolling 1100 aluminum alloy under a rolling load of 5500 lb per inch of strip width increased 10–15% when 4% polyalkylene glycol was added to the mineral oil base.

Another application for oil-soluble polyalkylene glycols is in vanishing oils. The polyalkylene glycols are dissolved in low molecular weight hydrocarbons having flash points below 140°F. The vanishing oil is then applied to the workpiece, where the volatile carrier evaporates, leaving a thin, uniform polyalkylene glycol film. This film provides excellent lubricity and is easy to remove from workpiece. In many cases the workpiece does not have to be cleaned.

Polyalkylene glycols, polyisobutylenes, and alkylbenzenes are all finding use in wire drawing compounds as carriers of dispersed solid lubricants. The major advantage of these synthetic lubricants in wire drawing operations consists of their clean burn-off characteristics during annealing [32,34].

Polyisobutylenes are also used as mineral oil thickeners in a wide variety of metalworking applications. Their high molecular weight, low staining characteristics, and tendency to volatilize completely at high temperatures without leaving varnishes make them well suited for this use [32].

There is little indication that straight oils containing synthetic lubricants are being used in

Copyright © 1999 Marcel Dekker, Inc.

**Table 24** Cutting Fluid Formulations Based on α-Olefins

| Component | Amount of component in formulation (wt %) | |
|---|---|---|
| | Formulation A (control) | Formulation B (α-olefin) |
| Paraffins[a] | 93 | 46.5 |
| α-Olefins | 0 | 46.5 |
| 1-Dodecanol | 6 | 6 |
| Butyl stearate | 1 | 1 |

[a]Equal amounts of $C_{16}$ and $C_{18}$ components were used.

cutting applications. The benefits associated with synthetic lubricants do not make up for the added cost in this segment of the metalworking industry. However, it is possible that poly(α-olefins) could be used as cutting oil base stocks in some specialty operations [34].

A relatively recent example of the use of synthetic lubricants in straight oil cutting fluids is the application of α-olefins containing 16–18 carbons as replacements for paraffin base stocks. The replacement of 50% of the paraffinic base stock with an α-olefin has been shown to increase the surface force of attraction to the metal surface by 10–40 percent [59,60]. This high surface attraction results in better surface finish and reduced tool wear. In some cases it has also enabled a reduction in the amount of sulfur-containing extreme pressure lubricity additives [59]. In sheet and foil rolling applications, increased thickness reductions, better surface finishes, and reductions in rolling force of up to 22% have been documented [59,61].

To demonstrate the advantages of using α-olefins in conjunction with paraffins in straight oil cutting fluids, the two test formulations shown in Table 24 were made up [60].

Formulations A and B were first evaluated by tapping predrilled holes in a piece of 1020 steel. The taps were then cleaned and examined for welding spots by means of a scanning electron microscope. The tap used with the paraffin-based formulation A showed 207 weld spots. The tap used with formulation B, where 50% of the paraffin base stock had been replaced with α-olefins, exhibited only 76 weld spots, a 63% reduction [62]. This reduction in welding results in longer tool life and better surface finish.

The same two formulations were then used to mill 356 and 380 aluminum alloys. The alloys were milled at a feed rate of 0.38 m/min. The cutting depth was set at $3.56 \times 10^{-4}$ m. After milling, the surfaces were examined for surface tears. The results are shown in Table 25 [60]. With both alloys, the use of formulation B containing the α-olefins resulted in significantly smoother surfaces that exhibited 20–30 percent less tearing.

**Table 25** Surface Finishes of Milled Aluminum Alloys

| Cutting fluid | Aluminum alloy | Torn area (%) |
|---|---|---|
| Formulation A | 356 | 69.4 |
| Formulation B | 356 | 53.4 |
| Formulation A | 380 | 83.7 |
| Formulation B | 380 | 58.7 |

Copyright © 1999 Marcel Dekker, Inc.

**Table 26** Surface Roughness of Turned 304 Stainless Steel Rod

| Cutting fluid | Tool type[a] | Tool speed (m/s) | Chip (μm) | Surface roughness (nm) | Standard deviation (nm) |
|---|---|---|---|---|---|
| Formulation A | HSS | 0.172 | 178 | 41.5 | 19.5 |
| Formulation B | HSS | 0.172 | 178 | 21.9 | 7.0 |
| Formulation A | CER | 2.34 | 152 | 63.3 | 26.4 |
| Formulation B | CER | 2.34 | 152 | 46.4 | 13.7 |
| Formulation A | CTD | 2.24 | 152 | 32.9 | 13.7 |
| Formulation B | CTD | 2.24 | 152 | 25.4 | 18.4 |

[a] HSS, high speed steel; CER, cermet; CTD, carbide insert coated with Ti nitride and Ti carbonitride.

Formulations A and B were also used to turn 304 stainless steel rods on a lathe. Three different cutting tools were used. The cutting conditions and test results are shown in Table 26 [60]. In all three cases, the use of the α-olefins in formulation B resulted in reduced surface roughness.

A second example of the use of synthetic lubricants in straight oil cutting fluids is the incorporation of the double-comb polymeric esters, which has been shown to improve the lubricity of metal cutting fluids, thereby improving tool life and surface finish [39].

Several formulations were made to determine the effectiveness of the double-comb polymeric esters in cutting fluids. These straight oil cutting fluids were evaluated by means of a tapping torque test machine. The effectiveness of the fluid can be determined by measuring the torque required to tap predrilled holes. The fluids were compared to a chloroparaffin-based reference oil. A "torque difference" was then calculated. A positive torque difference means that the test fluid outperformed the chloroparaffin standard by requiring less torque to tap a given hole. A negative torque difference indicates poorer fluid performance relative to the standard. The results, summarized in Table 27, show the benefits achieved through the use of the double-comb polymeric ester [39].

**Table 27** Cutting Fluid Formulations[a] Containing Double-Comb Polymeric Esters

| Formulation | Mineral oil (ISO VG 46) | TNPS* | Polymeric ester | TMP ester** | Torque difference |
|---|---|---|---|---|---|
| Chloroparaffin (reference) | — | — | — | — | — |
| Formulation Q | 100 | — | — | — | −3 |
| Formulation R | 98 | 2 | — | — | −0.50 |
| Formulation S | 75 | — | 25 | — | −0.25 |
| Formulation T | 73 | 2 | 25 | — | +0.30 |
| Formulation U | 73 | 2 | — | 25 | −1.15 |

[a] TNPS, di-*tert*-nonyl polysulfide (extreme pressure additives); TMP ester, $C_9$ fatty acid ester of trimethylolpropane.

Copyright © 1999 Marcel Dekker, Inc.

## IX. MARKET OUTLOOK

### A. Market Size

The total annual consumption of metalworking fluids in the United States is currently estimated to be between 100 and 140 million gallons of straight oils and water-dilutable concentrates [63,64]. Taking the dilution of the soluble oil, chemical, and semichemical concentrates into account, the total annual U.S. consumption of metalworking fluids has been estimated to be 3.2 billion gallons [65].

Approximately 60–70% of the metalworking fluids sold in the United States are used in metal removal operations, while the remaining metalworking fluids and concentrates are employed in forming applications [66,67].

It is estimated that 30–40% of these metalworking fluids sold in the United States are straight oils, while soluble oils, chemical, and semichemical fluid concentrates make up the remaining 60% [67]. The water-dilutable metalworking fluids can be subdivided further. Approximately 60% of these products are soluble oils, while the remaining 40% are divided between chemical and semichemical metalworking fluid concentrates [67]. Over the last several years, semisynthetic metalworking fluids have taken a greater share of this remaining 40% at the expense of true chemical solutions.

The growth rate of the metalworking fluid market in the United States has been slow over the last decade. Depending on the source, this market has grown at an annual rate between 0.1 and 1.3% [63,64,68]. It is expected that over the next 5 years the amount of metalworking fluids consumed in the United States will remain constant or even decrease slightly [64]. Environmental concerns will lead to the formulation of longer life fluids, characterized by improved fluid maintenance and increased recyclability. All these trends will contribute to a decrease in metalworking fluid consumption.

While the growth of the U.S. metalworking fluid market is slow or flat, the global use of metalworking lubricants appears to be growing significantly faster. Over the last 6 years the total global consumption of straight oil metalworking fluids and water-dilutable concentrates has grown from an estimated 474 million to 638 million gallons [67; unpublished data from Lubrizol Corp., 1996]. This represents a growth of 35%, or an annual growth rate of roughly 5%.

Approximately 40–50% of this 638 million gallons is straight oil metalworking fluids. Two-thirds of the remaining material is soluble oils, with semichemical fluids representing 10–20% of the total metalworking fluid market and chemical solutions accounting for only approximately 5% (unpublished data from Lubrizol Corp., 1996).

It is very difficult to determine the number of pounds of synthetic lubricants that go into each of the four segments of metalworking fluids. There are two major reasons for this. First, formulators hesitate to give out information regarding the amount of synthetic lubricants they use in order to protect their formulation strategies. Second, the producers of synthetic lubricants do not know what percentage of their products sold to formulators go into metalworking fluids. This is because the formulators of metalworking fluids are also likely to compound and sell other products like hydraulic fluids, gear lubricants, quenchants, and compressor lubricants. All these products can be formulated with synthetic lubricants, and it is therefore very difficult for polymer suppliers to identify all the applications in which their products are being used.

### B. Future of Synthetic Lubricants in Metalworking Fluids

Three major factors will influence the shape of the metalworking fluid market over the next decade. The first involves waste minimization, disposal, and environmental impact. The second factor is workpiece quality. The third is metalworking fluid toxicity.

Copyright © 1999 Marcel Dekker, Inc.

1. Waste Minimization and Disposal

The most important factor influencing the metalworking fluid market today is waste minimization and disposal. Waste disposal regulations are regional and vary considerably between municipalities. The appropriate choice of metalworking fluid may be greatly affected by these local regulations. The advantages and disadvantages of the four classes of metalworking fluids with respect to waste minimization and disposal are summarized in the paragraphs that follow.

Straight oil metalworking fluids are relatively easy to maintain. With the absence of water, and assuming that the product does not contain large amounts of fatty compounds, bacterial activity is minimal compared to water-based products. When the useful life of the straight oil metalworking fluid is over, the used product can be burned for fuel value or recycled [69]. However, the disposal of straight oil products can be made significantly more difficult by the presence of chlorinated paraffin lubricity additives. Also, stricter air quality standards are in some cases making it more difficult to use oil-based metalworking fluids because of mist formation, smoke generation, and the evolution of volatile hydrocarbons.

Of the water-based metalworking fluids, soluble oils are the most difficult to maintain. They are very susceptible to attack from microorganisms. They also tend to emulsify tramp oils and can be sensitive to water quality. Because they are two-phase systems, they are not always amenable to commonly used fluid maintenance techniques such as ion exchange, ultrafiltration, and centrifugation.

From a disposal point of view, soluble oils are relatively easy to treat. Soluble oils can be split rather easily into an oil phase, which can be incinerated or reclaimed, and a water phase. Often this water phase can be sent directly to the local publicly owned treatment works (POTW). However, as water regulations become stricter, there is an increase in the number of cases in which a fluid's aqueous phase fails to meet disposal regulations. In these cases, secondary treatment is required. Soluble oils that contain chlorinated paraffins are becoming more difficult to get rid of. It is becoming harder to incinerate chlorine-containing compounds, and local POTWs are starting to closely regulate the amount of chlorinated organic products that is accepted in a waste stream.

Chemical fluids are the easiest metalworking fluids to maintain. They are much more resistant to biological attack than soluble oils. Because they form true solutions in water, they are amenable to a wide variety of treatment techniques. They can be ion-exchanged to keep the water hardness under control, centrifuged to remove metal fines and tramp oils, and filtered to remove solids and emulsified oils. Large central systems containing chemical metalworking fluids have been maintained for periods of several years.

Because chemical metalworking fluids are easier to maintain than soluble oils, they generally last longer. This significantly reduces the volume of waste metalworking fluid that is generated. However, because all the components are water soluble, removing the organic components from the water is difficult. Whether this is a problem depends on the local regulations. Often a POTW will accept a spent chemical metalworking fluid if it is found to be compatible with the facility's treatment system. Sometimes a surcharge is levied.

Semichemical metalworking fluids fall somewhere between soluble oils and chemical products. They are usually easier to maintain than soluble oils. However, for disposal purposes, semichemical products often take on the worst characteristics of soluble oil and chemical metalworking fluids.

Much of the development work currently being done in the field of metalworking involves minimizing the environmental impact of the lubricants and coolants used to aid in the processing

Copyright © 1999 Marcel Dekker, Inc.

of the metal workpiece. The environmental impact of a metalworking fluid can be minimized by making formulation changes that extend the product's useful life or aid in its disposal.

A technology has recently been commercialized that may enable the formulation of soluble oils and semisynthetic metalworking fluids that exhibit both extended service life and cleaner, more efficient posttreatment and disposal. This technology is based on the development of a destructible, nonionic surfactant. Under basic conditions, this family of surfactants is stable and provides all the advantages of conventional nonionic surfactants. However, under acidic conditions, these surfactants readily and irreversibly split into their hydrophobic and hydrophilic constituents [70]. Once split, the surfactant can no longer effectively emulsify the oil phase of the metalworking fluid. The hydrophobic component of the splittable surfactant then separates out along with the hydrocarbon portion of the metalworking fluid. Once separated, the hydrophobic constituents of the metalworking fluid can be removed, resulting in a greatly reduced FOG (fats, oils, greases) content. The hydrophilic portion of the surfactant remains in the aqueous phase, which can be more easily handled because the hydrophobic components have been removed. Additionally, the treated aqueous phase has less environmental impact because the hydrophilic portion of the surfactant has faster biodegradation and lower aquatic toxicity than most common nonionic surfactants.

These splittable surfactants contain a pH-sensitive functionality [71,72] that serves to link the hydrophobic alkyl part of the surfactant to the hydrophilic alkoxylated portion. In a basic aqueous environment, such as that which exists in metalworking fluids, these surfactants are stable. However, if the solution is acidified, the pH-sensitive link becomes unstable and the surfactant breaks down into a hydrophobic compound and a hydrophilic alkoxylate. Since the surfactant is now destroyed, the emulsion separates. The hydrophobic segment of the surfactant separates out with the rest of the oil and can be removed from the aqueous portion of the metalworking fluid.

Surfactants are needed in soluble oil and semisynthetic metalworking fluids to emulsify hydrocarbon oils, which help to increase lubricity and corrosion protection. Anionic surfactants such as soaps and petroleum sulfonates are often used. This class of surfactant bears a negatively charged ion, which makes up the hydrophilic portion of the molecule. A commonly used treatment technology for used metalworking fluids is based on anionic surfactants; it involves the addition of acid and alum or a polyelectrolyte to neutralize the charge and thus remove the emulsifying properties of the surfactant [71]. The oil portion of the metalworking fluid then separates out and can be readily removed. The anionic surfactants, however, are prone to foaming and are sensitive to hard water.

Nonionic surfactants are often chosen over anionics for use in metalworking fluids because they have better wetting properties and are less sensitive to hard water [73]. Nonionic surfactants also allow the creation of tighter emulsions and are lower foaming that anionic surfactants [71]. The major problem with nonionic surfactants is that they are not amenable to treatment techniques commonly used to separate emulsions made with anionic surfactants.

The splittable nonionic surfactants provide the benefits of traditional nonionic surfactants while allowing the formulation of a soluble oil or semisynthetic metalworking that can be easily treated to enable the reduction of the FOG content prior to disposal. Treatment involves acidification of the metalworking fluid with sulfuric or hydrochloric acid to a pH of 3–5. The splitting of the acetal-based surfactant will increase in efficiency as the pH of the system decreases. The temperature of the system being treated should be between 20 and 50°C. Splitting efficiency will increase with increasing temperature. Deactivation time typically will range from 30 to 120 minutes, depending on the system and process conditions. Also, since the purpose of the splittable surfactant is to permit the coalescence of the FOGs into a readily removable form, the

Copyright © 1999 Marcel Dekker, Inc.

incorporation of other products that will act as surfactants or dispersants into the metalworking fluid should be avoided. Products that could impede the separation of the oil component of the metalworking fluid include polyacrylates, some phosphates, and conventional nonionic surfactants [71].

The splittable surfactants, like conventional nonionic surfactants, biodegrade at a moderate rate before being split. However, after being split in an acidic environment, the both hydrophilic and hydrophobic components exhibit much higher biodegradation rates [73].

The aquatic toxicity of the splittable surfactants before destruction is also similar to that of other nonionic surfactants. The hydrophilic component of the surfactant that results after splitting is essentially nontoxic to aquatic life. Most of the hydrophobe should be removed with the hydrocarbon phase of the acid treatment. Bacterial inhibition tests indicate that neither the surfactant nor its associated hydrophilic and hydrophobic components should negatively impact conventional biological wastewater treatment facilities when discharged at normally expected concentrations [73]. The aquatic toxicity of a splittable surfactant before and after acid treatment is shown in Table 28 [73].

2. Workpiece Quality

Product quality is becoming extremely important. As a result, tolerance of workpiece corrosion, staining, and coating defects is decreasing. Two major causes of staining and coating defects are the presence of corrosive additives in the metalworking fluid and the incomplete removal of the lubricant prior to the coating process.

Chlorinated hydrocarbons are one of the most commonly used EP lubricity additives in straight oil and soluble oil metalworking fluids. However, during storage, the residual chlorine can cause significant staining of the metal workpieces. Because of their staining tendencies and because their disposal is becoming increasingly difficult, much work is under way to develop replacements. This work is providing significant opportunities for the use of synthetic lubricants in metalworking fluids.

The complete removal of residual metalworking fluids from the workpiece can be difficult when either straight oil or soluble oil products are used. Residual lubricant can prevent the adherence of coatings, like paint or enamel, causing unacceptable defects. These problems are becoming more widespread as the use of vapor degreasers and solvent cleaning processes are coming under pressure for various environmental reasons. The need for water-washable metalworking fluids should result in the increased use of chemical and semichemical products. It will also favor the use of neat polyalkylene glycols in straight oil applications, where solvent cleaning operations can be omitted because of the polymer's water solubility. The complete burn-off

**Table 28** Aquatic Toxicity[a] of a Splittable Acetal-Based Nonionic Surfactant (9 mol ethoxylate)

| Surfactant | Acute *Daphnia magna*, 48 h $LC_{50}$ (mg/L) | Acute fathead minnow, 96 h $LC_{50}$ (mg/L) | Bacterial inhibition, 16 h $IC_{50}$ (mg/L) | Selenastrum algal, 96 h $EC_{50}$ (mg/L) |
|---|---|---|---|---|
| Before acid treatment | 15 | 5 | >10,000 | 6 |
| After acid treatment | | | | |
| Hydrophobe | 0.3 | 2 | 970 | 0.5 |
| Hydrophile | 10,000 | >10,000 | >10,000 | >20,000 |

[a] $LC_{50}$, median lethal concentration; $IC_{50}$, inhibition concentration; $EC_{50}$, calculated concentration with expected algal cell counts at 50% of control cell counts.

Copyright © 1999 Marcel Dekker, Inc.

characteristics of polyalkylene glycols, polyisobutylenes, and alkylbenzenes will become more important, since they sometimes enable the elimination of a cleaning step prior to various high temperature operations.

As the need for improved workpiece quality grows, the production of defective parts will become unacceptable. The resistance to the higher price of synthetic lubricants should therefore decrease as the cost associated with seconds due to inadequate cleaning increases.

3. Toxicity

Health concerns are very important in the metalworking industry because of the high exposure of the operator to the metalworking fluids. Potential carcinogens such as polycyclic aromatic hydrocarbons [74], nitrosamines, and specific short chain chlorinated paraffins have been successfully eliminated from use in metalworking fluid formulations [75]. Studies are currently under way to promote better understanding of the health effects of other chemicals commonly used in metalworking fluids, including biocides [76,77], formaldehyde [78], diethanolamine, *o*-phenylphenol, and oil mists [79]. Bacterial growth in metalworking fluids and the resulting endotoxin production is also receiving attention, especially the role of endotoxin concentration in respiratory distress [75].

In general, synthetic lubricant base stocks are very pure relative to petroleum oil basestocks and are therefore less likely to contain potentially undesirable impurities. Also, synthetic lubricant base stocks such as poly(α-olefins) [80], polyalkylene glycols [81], and polyolesters [82] exhibit low orders of toxicity via skin absorption or ingestion. Some PAOs and polyalkylene glycols have been cleared by the U.S. Food and Drug Administration for various applications [81]. The high purity and low toxicity of these synthetic lubricant base stocks could lead to the increased usage of the products as the effort to understand the health effects of metalworking fluids is increased. However, it is difficult to foresee the next toxicity issue or to predict how it will affect the use of synthetic lubricants in the metalworking industry.

## X. CONCLUSIONS

Synthetic lubricants will continue to play a major role as water-soluble lubricity additives in chemical and semichemical metalworking fluids. The synthetic lubricants most commonly used in these metalworking fluids are polyalkylene glycols and their ester or acid derivatives. Metalworking fluids based on these products are excellent coolants and lubricants. They are in general easy to maintain, low in toxicity and environmental impact, nonstaining, and easy to remove from the finished workpiece. As environmental issues become more important, the use of this class of synthetic lubricants in metalworking fluids is likely to increase.

In straight oil metalworking fluids, the use of synthetic lubricants is basically limited to specialty applications. Synthetic esters, polyisobutylenes, and polyalkylene glycols are all used in applications where clean burn-off or nonstaining characteristics are important.

The use of synthetic lubricants in metalworking fluids will grow. Increasingly strict environmental regulations affecting the workplace and air and water quality will favor the use of water-based products and therefore polyalkylene glycol lubricants. Environmental and disposal-related concerns will also reduce the use of solvent cleaning systems and chlorinated lubricity additives. Both these factors should also favor the use of synthetic lubricants. The emphasis on product quality and the increasing cost of seconds will also increase the consumption of synthetic lubricants. As the costs associated with waste disposal, fluid maintenance, and workpiece quality all increase, the performance advantages of synthetic lubricants will outweigh their higher initial price and lead to their increased application in metalworking lubricants.

Copyright © 1999 Marcel Dekker, Inc.

## ACKNOWLEDGMENTS

I gratefully acknowledge the contributions and guidance I received from Dr. Paul L. Matlock and Dr. Nye A. Clinton. I especially thank my wife Kathy for her support, advice, and technical input. I also thank my sons Robby and Tommy for their patience during the writing of this chapter.

## REFERENCES

1. Shaw, M. C., *Metal Cutting Principles,* 3rd ed., MIT Press, Cambridge, MA, 1957.
2. Schey, J. A., *Tribology in Metalworking,* American Society for Metals, Metals Park, OH, 1983.
3. Ellis, E. G., *Fundamentals of Lubrication,* Scientific Publications (G.B.) Ltd., Broseley, Shropshire, 1968.
4. Booser, R. E., *Handbook of Lubrication,* Vol. II, CRC Press, Boca Raton, FL, 1988.
5. Springborn, R. K., *Cutting and Grinding Fluids: Selection and Application,* American Society of Tool and Manufacturing Engineers, Dearborn, MI, 1967.
6. Kajdas, C., Additives for metalworking lubricants—A review, *Lubr. Sci., 1,* 385–409 (1989).
7. Robin, M., Forming with water base lubricants, *Manuf. Eng., 81,* 53–55 (1978).
8. Barber, S. J., and Millett, W. H., Water: "New" metalworking solution? *Am. Mach., 118,* 95–100 (1974).
9. Evans, E. A., *Lubricating and Allied Oils,* Chapman & Hall Ltd., London, 1963.
10. Biringuccio, V., *The Pirotechnia of Vannoccio Biringuccio (1540)* (C. L. Smith and M. T. Gnudi, transl.), Basic Books, New York, 1959.
11. Northcott, W. H., *A Treatise on Lathes and Turning,* Longmans, Green & Co., London, 1868.
12. Edwards, J., and Jones, E., Synthetic cutting fluids, *Tribol. Int., 10,* 29–31 (1977).
13. Kelly, R., Synthetic can-drawing fluids for D & I operations, *Lubr. Eng., 38,* 675–680 (1982).
14. Morton, I. S., Water base cutting fluids still a ?, *Ind. Lubr. Tribol., 23,* 57–62 (1971).
15. Taylor, F. W., On the art of cutting metals, *Trans. ASME, 28,* 31–58 (1907).
16. Beaton, J., Tims, J. M., and Tourret, R., Function of metal-cutting fluids and their mode of action, *Proc. Inst. Mech. Eng., 170,* 193–214 (1964–1965).
17. Sluhan, C. A., Cutting fluids, *Am. Soc. Tool Manuf. Eng., 62* (399), (1963).
18. Thomhill, F. H., Synthetic cutting oils, *Ind. Lubr. Tribol., 23,* 70–72 (1971).
19. Langer, T. W., and Blake, F. M., Inhibited polyoxyalkylene glycol fluids, U.S. Patent 2,624,708 (1953).
20. Mould, R. W., Silver, H. B., and Syrett, R. J., Investigations of the activity of cutting oil additives: V. The EP activity of some water-based fluids, *Lubr. Eng., 33,* 291–298 (1977).
21. Sluhan, C. A., Some considerations in the selection and use of water soluble cutting and grinding fluids, *Lubr. Eng., 16,* 110–118 (1960).
22. Hunz, R. P., Water-based metalworking lubricants, *Lubr. Eng., 40,* 549–553 (1984).
23. *American Machinist,* Manufacturing Research Institute, Data Sheet MRI-12.
24. Mueller, E. R., and Martin, W. H., Polyalkylene glycol lubricants: Uniquely water soluble, *Lubr. Eng., 31,* 348–356 (1975).
25. Jarvholm, B., Zingmark, P. A., and Osterdahl, B. G., High concentration of *n*-nitrosodiethanolamine in a diluted commercial cutting fluid, *Am. J. Ind. Med., 19,* 237–239 (1991).
26. U.S. Environmental Protection Agency, Notice to formulators of metalworking fluids—Potential risk from nitrosamines, *EPA Chemical Advisory,* TS-799, September 1984.
27. Ladov, E. N., Evaluating and communicating the carcinogenic hazards of petroleum derived lubricant base oils and products, *Lubr. Eng., 42,* 272–277 (1986).
28. Klamann, D., *Lubricants and Related Properties,* Verlag Chemie, Deerfield Beach, FL, 1984.
29. Mullins, R. M., Miller, P. R., and Bucko, R. J., A comparison of matrix and nonmatrix tapping torque test procedures in the evaluation of experimental cutting fluids, ASLE Preprint 84-AM-3C-1 (1984).

Copyright © 1999 Marcel Dekker, Inc.

30. Brown, W. L., The role of polyalkylene glycols in synthetic metalworking fluids, *Lubr. Eng., 44,* 168–171 (1988).
31. Whetzel, J. C., Jr., Chapel, F., and Rodman, S., Metal working lubricant, U.S. Patent 3,124,531 (1964).
32. Singh, R. V., Synthetic metal working lubricants, *3rd Internationales Kolloquium, Schmierstoffe in der Metallbearbeitung, 1,* 32.1–32.7 (1982).
33. Przybylinski, J. L., Diethanol disulfide as an extreme pressure and anti-wear additive in water soluble metalworking fluids, U.S. Patent 4,250,046 (1981).
34. Williamson, E. I., Commercial developments in synthetic lubricants—A European overview, part 2, *J. Synth. Lubr., 3,* 45–53 (1986).
35. Russ, J. M., Jr., "UCON" synthetic lubricants and hydraulic fluids, ASTM Technical paper 77:3–11, American Society for Testing and Materials, Philadelphia, 1947.
36. Canter, N. M., Chaloupka, J. J., and Fischesser, G. J., The use of ethylene oxide/propylene oxide (EO/PO) esters as additives in semisynthetic metalworking formulations, *Lubr. Eng., 44,* 257–261 (1988).
37. Sweatt, C. H., and Langer, T. W., Some industrial experiences with synthetic lubricants, *Mech. Eng., 73,* 469–476 (1951).
38. Miller, P. R., and Patel, H., Using complex polymeric esters as multifunctional replacements for chlorine and other additives in metalworking, *Lubr. Eng., 53,* 31–33 (1997).
39. Akzo, Ketjenlube 115, 135, and 165—A new and proven approach to wear reduction. Technical literature 89.08.10034, Akzo Chemicals, Chicago, 1989.
40. Hobson, P. D., *Industrial Lubrication Practice,* Industrial Press, New York. 1955.
41. Beiswanger, J. P. G., Katzenstein, W., and Krupin, F., Phosphate ester acids as load-carrying additives and rust inhibitors for metalworking fluids, *ASLE Trans., 7,* 398–405 (1964).
42. Smith, G. F., and Budd, M. K., Lubricants for cold working of aluminum, U.S. Patent 3,966,619 (1976).
43. Mateeva, S., and Glavchev, I., Some operational characteristics of a hydrolysed polyacrylonitrile-based cutting fluid, *Tribol. Int., 13,* 69–71 (1980).
44. Stram, M. A., Lubricant compositions, U.S. Patent 3,657,123 (1972).
45. Grower, H. D., Grower, B. G., and Young, D., Aqueous lubricating compositions containing salts of styrene-maleic anhydride copolymers and an inorganic boron compound, U.S. Patent 3,629,112 (1971).
46. Janatka, V., and Kirwan, E. P., Lubricant-coolant, U.S. Patent 3,563,859 (1971).
47. Marx, J., Synthetic lubricant for machining and chipless deformation of metals, U.S. Patent 3,980,571 (1976).
48. Felton, G. F., Jr., Low smoking lubricating composition for cold heading operations, U.S. Patent 3,983,044 (1976).
49. Guminski, R. D., and Willis, J. J., Development of cold-rolling lubricants for aluminum alloys, *J. Inst. Met, 88,* 481–492 (1960).
50. Richter, J. P., Cutting oil performance—A significant new machining test, ASLE preprint 77-LC-2C-3 (1977).
51. DeChiffre, L., Lubrication in cutting—Critical review and experiments with restricted contact tools, *ASLE Trans., 24,* 340–344 (1980).
52. Ham, I., Fundamentals of tool wear, *American Society of Tool and Manufacturing Engineers,* MR68–617 (1968).
53. Brown, W. L., Notebook 12811, Union Carbide Chemicals and Plastics Company, Inc., unpublished (1987).
54. Nash, J. C., and Colakovic, N., Effect of synthetic additives on the performance of aluminum tapping fluids, *Lubr. Eng., 41,* 721–724 (1985).
55. Levesque, A., and McCabe, M., Improved synthetic coolants using a modified polyalkylene glycol, *Lubr. Eng., 40,* 664–666 (1984).
56. Faville, W. A., and Voitik, R. M., The Falex tapping torque test machine, *Lubr. Eng., 34,* 193–197 (1978).

Copyright © 1999 Marcel Dekker, Inc.

57. Katsuki, A., Ueno, T., Matsuoka, H., and Kohara, M., Research on soluble cutting fluids for gear cutting—The influence of dilution ratio and the effect of synthetic fluids, *Jpn. Soc. Mech. Eng., 28,* 735–743 (1985).
58. Brown, W. L., The use of polyalkylene glycols in metal forming and drawing lubricants, *STLE Annual Meeting,* Denver, 1990.
59. Shell, NEODENE alpha olefins for metalworking lubricants, Technical literature SC: 1927–94R, Shell Chemical Company, Houston, TX, 1994.
60. Denley, D. R., York, G., and Haberman, L. M., Olefinic versus paraffinic based fluids in metalworking applications probed by three different microscopic techniques, Technical bulletin SC:2208–94, Shell Chemical Company, Houston, TX, 1994.
61. Koyama, S., Shido, S., Onodera, X., Hara, S., Tomari, Y., Saito, T., and Nara, T.; Lubricating oil composition, U.S. Patent 5,171,903 (1992).
62. Shell, NEODENE additives for metalworking fluids, Technical literature SC:2222-95, Shell Chemical Company, Houston, TX, 1995.
63. ILMA, Report on the Volume of Lubricants Manufactured in the *United States and Canada by Independent Lubricant Manufacturers in 1995,* Independent Lubricant Manufacturers Association, Alexandria, VA, 1996.
64. The Fredonia Group, Inc., Marketing news—Demand for industrial lubricants reach 1.3 billion gallons in 2000, *Lubr, Ing., 52,* 391 (1996).
65. Anon., HWB fluid market seen ready for sharp growth, *Chem. Marketing Rep. 227,* 27 (1985).
66. National Petroleum Refiners Association, *1989 Report on U.S. Lubricating Oil Sales,* NPRA, Washington, DC, 1989.
67. The Lubrizol Corp. *Metalworking Fluid Trends,* Lubrizol document 491 404–7 (1991).
68. Steigerwald, J. C., *Report on the Volume of Lubricants Manufactured by the Independent Lubricant Manufacturers in 1989,* Independent Lubricant Manufacturers Association, Alexandria, VA, 1989.
69. Childers, J. C., Metalworking fluids—A geographical industry analysis, *Metalwork. Topi, 1*(2), 1–4 (1989).
70. Anon., Product report, EPA endorses Union Carbide surfactant, *Chem. Eng. News, 75*(4), 44 (1997).
71. Galante, D. C., Hoy, R. C., Joseph, A. F., King, S. W., Smith, C. A., and Wizda, C. M., Aldehyde-based surfactant and method for treating industrial, commercial, and institutional waste-water, European Patent Application EP 0742177-A1 (1996).
72. Galante, D. C., Hoy, R. C., Joseph, A. F., King, S. W., Smith, C. A., and Wizda, C. M., Ketone-based surfactant and method for treating industrial, commercial, and institutional waste-water, European Patent Application EP 0742178-A1 (1996).
73. Union Carbide, Triton® SP-series surfactants, Technical literature UC-1492, Union Carbide Corp., Danbury, CT, 1996.
74. McKee, R. H., and O'Connor, D. J., Dermal carcinogenicity studies of metalworking fluids, *Lubr. Eng., 52,* 97–102 (1996).
75. Rossmore, H. W., Health and environment, *Lubr. Eng., 52,* 94–96 (1996).
76. Passman, F. J., Formaldehyde risk in perspective: A toxicological comparison of twelve biocides, *Lubr. Eng., 52,* 69–80 (1996).
77. Rossmore, H. W., and Rossmore, L. A., Factors affecting selection of metalworking fluid biocides, *Lubr. Eng., 52,* 23–28 (1996).
78. Brutto, P. E., Pohlman, J. L., Ryan, A. M., and Smith, R., Formaldehyde control in metalworking fluids preserved with triazine biocide, *Lubr. Eng., 52,* 8–14 (1996).
79. Lucke, W. E., Health and safety of metalworking fluids, *Lubr. Eng., 52,* 596–604 (1996).
80. Booser, R. E., *CRC Handbook of Lubrication and Tribology, Vol. III,* CRC Press, Boca Raton, FL, 1994.
81. Shubkin, R. L., ed., *Synthetic Lubricants and High-Performance Functional Fluids,* 1st ed., Dekker, New York, 1993.
82. Henkel, Emery 2941-B ISO 46 synthetic lubricant (basestock), Material Safety Data Sheet (MSDS) 2941-B, Henkel Corp.–Emery Group, Cincinnati, OH, 1994.

Copyright © 1999 Marcel Dekker, Inc.